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(21) International Application Number: PCT/US99/24823 (22) International Filing Date: 22 October 1999 (22.10.99) (30) Priority Data: 60/105,380 23 October 1998 (23.10.98) US (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): MIRACLE, Gregory, Scot [US/US]; 3065 Old Oxford Road, Hamilton, OH 45013 (US). PRICE, Kenneth, Nathan [US/US]; 265 Compton Road, Wyoming, OH 45215 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).		(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: FRAGRANCE PRO-ACCORDS AND ALDEHYDE AND KETONE FRAGRANCE LIBRARIES (57) Abstract The present invention relates to novel heterocyclic pro-fragrances, preferably oxazolidines, tetrahydro-1,3-oxazines, thiazolidines, or tetrahydro-1,3-thiazines, more preferably oxazolidines, or tetrahydro-1,3-oxazines, most preferably oxazolidines, which are capable of sustained release of fragrance raw material ketones and aldehydes and to fragrance delivery systems which comprise saidpro-fragrances.		

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FRAGRANCE PRO-ACCORDS AND ALDEHYDE AND KETONE FRAGRANCE LIBRARIES

FIELD OF THE INVENTION

The present invention relates to novel fragrance pro-accords which release fragrance raw material aldehydes and ketones suitable for use in perfume and fine fragrance compositions thereby providing said compositions with enduring fragrance characteristics. The present invention further relates to a fragrance delivery system which comprises the novel fragrance pro-accords of the present invention in combination with a) one or more pro-accords *inter alia* acetals, ketals, orthoesters, orthocarbonates, and b) one or more fragrance raw materials.

BACKGROUND OF THE INVENTION

Humans have applied scents and fragrances to their skin since antiquity. Originally these aesthetically pleasing materials were commonly isolated in raw form as resins, gums or essential oils from natural sources, *inter alia*, the bark, roots, leaves and fruit of indigenous plants. These resins, gums, and oils were directly applied to the body or diluted with water or other solvent, including in some cases, wine. With the advent of modern chemistry, individual components responsible for the odor properties of these resins, gums and oils were isolated and subsequently characterized. Aside from common "perfume vehicles" *inter alia*, fine perfumes, colognes, eau de toilettes, and after-shave lotions, a wide variety of personal care or personal hygiene items also deliver for aesthetic reasons fragrance notes, accords, or fragrance "characteristics".

It is well known that mixtures of perfume or fragrance raw materials when deposited on the skin lose intensity and may change character with time, mainly due to factors such as differential evaporation and skin penetration. Many attempts have been made to minimize these drawbacks, but so far without notable success. Particularly, efforts have been made to prolong the diffusion, as well as to improve other characteristics of fragrance materials, by e.g. increasing the fragrance raw material concentration or by using additives such as silicones, glycerol, polyethylene glycols and so on. Such additions, however, have never been adequate to increase the longevity of the fragrance odor.

In addition to alcohols and esters, aldehydes and ketones form the most commonly delivered fragrance raw materials. Alcohols and esters can be suitably released in a delayed

manner from an orthoester pro-accord or pro-fragrance. The controllable release of these fragrance raw materials thus provides the formulator with a means for delivering these fragrance ingredients, not only as an accord, but in a delayed-releasable manner over a period of time fragrance which is desirable to the fine fragrance and perfume user. However, the primary means for delivering aldehydes and ketones in a time-releasable manner has typically been the acetal and ketal pro-fragrance. Notwithstanding the fact that these materials are capable of delivering the required aldehyde and ketone under the proper acidic conditions, in the past, because there was no means of adjusting the release profiles of pro-fragrances, these compounds have not provided the formulator with a highly controllable method for sustained and predictable delivery of aldehydes and ketones.

Accordingly, there remains a need in the art for a pro-accord which can be formulated into fine fragrances, perfumes, personal care and personal hygiene products wherein aldehyde and ketone fragrance raw material components can be released in a highly controllable manner to provide enhanced fragrance longevity.

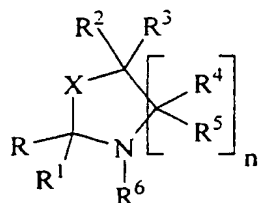
SUMMARY OF THE INVENTION

The present invention meets the aforementioned needs in that it has been surprisingly discovered that aldehyde and ketone fragrance raw materials can be controllably released from novel heterocyclic pro-accords or pro-fragrances. The novel pro-fragrances or pro-accords of the present invention are heterocycles, preferably oxazolidines, tetrahydro-1,3-oxazines, thiazolidines, or tetrahydro-1,3-thiazines, more preferably oxazolidines, or tetrahydro-1,3-oxazines, most preferably oxazolidines. These pro-fragrances provide controllable release of fragrance raw materials and thereby enhance the longevity of perfumes and fragrances when applied to human skin. The pro-accords or pro-fragrances of the present invention can be easily formulated into any type of personal care or personal hygiene articles *inter alia* fine fragrances, perfumes, deodorants, body lotions or creams, ointments, balms, salves, antiseptics, suntan lotions, or shampoos.

The pro-fragrances and/or pro-accords described herein comprise fragrance raw materials in a stable, releasable "pro-fragrance" form. In general, the pro-fragrances can be formulated into any product which is deliverable to human skin, directly or indirectly, provided the product pH, carriers and adjunct materials are compatible with the pro-fragrance chemical form. Once in contact with human skin, the heterocyclic pro-fragrance releases a fragrance raw material at a rate which provides extended fragrance benefits. The fragrance delivery systems of

the present invention can be a mixture of any number of pro-fragrances or pro-accords and can cover any fragrance "characteristic" or desired fragrance volatility.

The first aspect of the present invention relates to a pro-fragrance or pro-accord having the formula:



wherein said pro-fragrance or pro-accord releases an aldehyde or a ketone fragrance raw material, wherein X is oxygen or sulfur; R is:

- a) C₆-C₂₂ substituted or unsubstituted linear alkyl;
- b) C₆-C₂₂ substituted or unsubstituted branched alkyl;
- c) C₆-C₂₂ substituted or unsubstituted linear alkenyl;
- d) C₆-C₂₂ substituted or unsubstituted branched alkenyl;
- e) C₆-C₂₂ substituted or unsubstituted cycloalkyl;
- f) C₆-C₂₂ substituted or unsubstituted branched cycloalkyl;
- g) C₆-C₂₂ substituted or unsubstituted cycloalkenyl;
- h) C₆-C₂₂ substituted or unsubstituted branched cycloalkenyl;
- i) C₆-C₂₂ substituted or unsubstituted aryl;
- j) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- k) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;
- l) and mixtures thereof;

R¹ is:

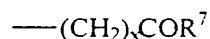
- a) hydrogen;
- b) C₁-C₁₀ substituted or unsubstituted linear alkyl;
- c) C₃-C₁₀ substituted or unsubstituted branched alkyl;
- d) C₂-C₁₀ substituted or unsubstituted linear alkenyl;
- e) C₃-C₁₀ substituted or unsubstituted branched alkenyl;
- f) C₃-C₁₅ substituted or unsubstituted cycloalkyl;
- g) C₄-C₁₅ substituted or unsubstituted branched cycloalkyl;
- h) C₄-C₁₅ substituted or unsubstituted cycloalkenyl;
- i) C₅-C₁₅ substituted or unsubstituted branched cycloalkenyl;

- j) C₆-C₁₅ substituted or unsubstituted aryl;
- k) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- l) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;
- m) and mixtures thereof;

R and R¹ can be taken together to form a substituted or unsubstituted ring having in the ring from 3 to 10 carbon atoms;

each R², R³, and each R⁴ and R⁵ pair are independently:

- a) R¹;
- b) hydroxyl;
- c) a carbonyl comprising unit having the formula:



wherein R⁷ is:

- i) -OH;
- ii) -OR⁸ wherein R⁸ is hydrogen, C₁-C₁₅ substituted or unsubstituted linear alkyl, C₁-C₁₅ substituted or unsubstituted branched alkyl, C₂-C₂₂ substituted or unsubstituted linear alkenyl, C₃-C₂₂ substituted or unsubstituted branched alkenyl, or mixtures thereof, wherein said substitution is not halogen;
- iii) -N(R⁹)₂ wherein R⁹ is hydrogen, C₁-C₆ substituted or unsubstituted linear alkyl, C₃-C₆ substituted or unsubstituted branched alkyl, or mixtures thereof;
- iv) C₁-C₂₂ substituted or unsubstituted linear alkyl;
- v) C₁-C₂₂ substituted or unsubstituted branched alkyl;
- vi) C₂-C₂₂ substituted or unsubstituted linear alkenyl;
- vii) C₃-C₂₂ substituted or unsubstituted branched alkenyl;
- viii) C₃-C₂₂ substituted or unsubstituted cycloalkyl;
- ix) C₆-C₂₂ substituted or unsubstituted aryl;
- x) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- xi) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;

the index x is from 1 to 22;

- d) alkyleneoxy units having the formula:



wherein each R¹⁰, R¹¹, and R¹² is independently:

- i) hydrogen;
- ii) -OH;
- iii) C₁-C₄ alkyl;
- iv) or mixtures thereof;

R¹³ is:

- i) hydrogen;
- ii) C₁-C₄ alkyl;
- iii) or mixtures thereof;

R¹⁴ is:

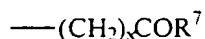
- i) hydrogen;
- ii) C₁-C₄ alkyl;
- iii) or mixtures thereof;

R¹⁰ and R¹¹ can be taken together to form a C₃-C₆ spiroannulated ring, carbonyl unit, or mixtures thereof; y has the value from 0 to 10, z has the value from 1 to 50;

- e) and mixtures thereof;

R⁶ is:

- a) C₁-C₁₀ substituted linear alkyl;
- b) C₃-C₁₀ substituted branched alkyl;
- c) C₂-C₁₀ substituted or unsubstituted linear alkenyl;
- d) C₃-C₁₀ substituted or unsubstituted branched alkenyl;
- e) C₃-C₁₅ substituted cycloalkyl;
- f) C₄-C₁₅ substituted or unsubstituted branched cycloalkyl;
- g) C₄-C₁₅ substituted or unsubstituted cycloalkenyl;
- h) C₅-C₁₅ substituted or unsubstituted branched cycloalkenyl;
- i) C₆-C₁₅ substituted aryl;
- j) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- k) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;
- l) a carbonyl comprising unit having the formula:



wherein R⁷ is:

- i) -OH;

- ii) $-OR^8$ wherein R^8 is hydrogen, C_1-C_{15} substituted linear alkyl, $C_{11}-C_{15}$ unsubstituted linear alkyl, C_1-C_{15} substituted branched alkyl, $C_{11}-C_{15}$ unsubstituted branched alkyl, C_2-C_{22} substituted or unsubstituted linear alkenyl, C_3-C_{22} substituted or unsubstituted branched alkenyl, or mixtures thereof, wherein said substitution is not halogen or thioalkyl;
 - iii) $-N(R^9)_2$ wherein R^9 is hydrogen, C_1-C_6 substituted or unsubstituted linear alkyl, C_3-C_6 substituted or unsubstituted branched alkyl, or mixtures thereof;
 - iv) C_1-C_{22} substituted or unsubstituted linear alkyl;
 - v) C_1-C_{22} substituted or unsubstituted branched alkyl;
 - vi) C_2-C_{22} substituted or unsubstituted linear alkenyl;
 - vii) C_3-C_{22} substituted or unsubstituted branched alkenyl;
 - viii) C_3-C_{22} substituted or unsubstituted cycloalkyl;
 - ix) C_6-C_{22} substituted or unsubstituted aryl;
 - x) C_6-C_{22} substituted or unsubstituted heterocyclicalkyl;
 - xi) C_6-C_{22} substituted or unsubstituted heterocyclicalkenyl;
- the index x is from 0 to 22;

m) alkyleneoxy units having the formula:



wherein each R^{10} , R^{11} , and R^{12} is independently;

- i) hydrogen;
- ii) $-OH$;
- iii) C_1-C_4 alkyl;
- iv) or mixtures thereof;

R^{13} is:

- i) hydrogen;
- ii) C_1-C_4 alkyl;
- iii) or mixtures thereof;

R^{14} is:

- i) hydrogen;
- ii) C_1-C_4 alkyl;
- iii) or mixtures thereof;

R¹⁰ and R¹¹ can be taken together to form a C₃-C₆ spiroannulated ring, carbonyl unit, or mixtures thereof; y has the value from 0 to 10, z has the value from 1 to 50:

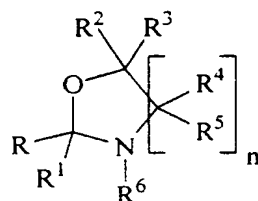
n) and mixtures thereof;

any two R^2 , R^3 , R^4 , R^5 , or R^6 units can be taken together to form:

- i) a carbonyl moiety;
- ii) a C₃-C₆ spiroannulated ring;
- iii) a heterocyclic aromatic ring comprising from 5 to 7 atoms;
- iv) a non-heterocyclic aromatic ring comprising from 5 to 7 atoms;
- v) a heterocyclic ring comprising from 5 to 7 atoms;
- vi) a non-heterocyclic ring comprising from 5 to 7 atoms;
- vii) or mixtures thereof; and

the index n is an integer from 1 to 3.

A second aspect of the present invention relates to fragrance delivery systems which comprise a pro-fragrance or pro-accord having the formula:



wherein said pro-fragrance or pro-accord releases an aldehyde or a ketone fragrance raw material, wherein X is oxygen or sulfur; R is:

- a) C₆-C₂₂ substituted or unsubstituted linear alkyl;
- b) C₆-C₂₂ substituted or unsubstituted branched alkyl;
- c) C₆-C₂₂ substituted or unsubstituted linear alkenyl;
- d) C₆-C₂₂ substituted or unsubstituted branched alkenyl;
- e) C₆-C₂₂ substituted or unsubstituted cycloalkyl;
- f) C₆-C₂₂ substituted or unsubstituted branched cycloalkyl;
- g) C₆-C₂₂ substituted or unsubstituted cycloalkenyl;
- h) C₆-C₂₂ substituted or unsubstituted branched cycloalkenyl;
- i) C₆-C₂₂ substituted or unsubstituted aryl;
- j) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- k) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;

l) and mixtures thereof;

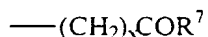
R¹ is:

- a) hydrogen;
- b) C₁-C₁₀ substituted or unsubstituted linear alkyl;
- c) C₃-C₁₀ substituted or unsubstituted branched alkyl;
- d) C₂-C₁₀ substituted or unsubstituted linear alkenyl;
- e) C₃-C₁₀ substituted or unsubstituted branched alkenyl;
- f) C₃-C₁₅ substituted or unsubstituted cycloalkyl;
- g) C₄-C₁₅ substituted or unsubstituted branched cycloalkyl;
- h) C₄-C₁₅ substituted or unsubstituted cycloalkenyl;
- i) C₅-C₁₅ substituted or unsubstituted branched cycloalkenyl;
- j) C₆-C₁₅ substituted or unsubstituted aryl;
- k) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- l) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;

R and R¹ can be taken together to form a substituted or unsubstituted ring having in the ring from 3 to 10 carbon atoms; and

each R², R³, R⁶ and each R⁴ and R⁵ pair are independently:

- a) R¹;
- b) hydroxyl;
- c) a carbonyl comprising unit having the formula:



wherein R⁷ is:

- i) -OH;
- ii) -OR⁸ wherein R⁸ is hydrogen, C₁-C₁₅ substituted or unsubstituted linear alkyl, C₁-C₁₅ substituted or unsubstituted branched alkyl, C₂-C₂₂ substituted or unsubstituted linear alkenyl, C₃-C₂₂ substituted or unsubstituted branched alkenyl, or mixtures thereof;
- iii) -N(R⁹)₂ wherein R⁹ is hydrogen, C₁-C₆ substituted or unsubstituted linear alkyl, C₃-C₆ substituted or unsubstituted branched alkyl, or mixtures thereof;
- iv) C₁-C₂₂ substituted or unsubstituted linear alkyl;
- v) C₁-C₂₂ substituted or unsubstituted branched alkyl;
- vi) C₂-C₂₂ substituted or unsubstituted linear alkenyl;

- vii) C₃-C₂₂ substituted or unsubstituted branched alkenyl;
- viii) C₃-C₂₂ substituted or unsubstituted cycloalkyl;
- ix) C₆-C₂₂ substituted or unsubstituted aryl;
- x) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- xi) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;

the index x is from 0 to 22;

- d) alkyleneoxy units having the formula:



wherein each R¹⁰, R¹¹, and R¹² is independently;

- i) hydrogen;
- ii) -OH;
- iii) C₁-C₄ alkyl;
- iv) or mixtures thereof;

R¹³ is:

- i) hydrogen;
- ii) C₁-C₄ alkyl;
- iii) or mixtures thereof;

R¹⁴ is:

- i) hydrogen;
- ii) C₁-C₄ alkyl;
- iii) or mixtures thereof;

R¹⁰ and R¹¹ can be taken together to form a C₃-C₆ spiroannulated ring, carbonyl unit, or mixtures thereof; y has the value from 0 to 10, z has the value from 1 to 50;

- e) any two R², R³, R⁴, R⁵, or R⁶ units can be taken together to form:
- i) a carbonyl moiety;
 - ii) a C₃-C₆ spiroannulated ring;
 - iii) a heterocyclic aromatic ring comprising from 5 to 7 atoms;
 - iv) a non-heterocyclic aromatic ring comprising from 5 to 7 atoms;
 - v) a heterocyclic ring comprising from 5 to 7 atoms;
 - vi) a non-heterocyclic ring comprising from 5 to 7 atoms;
 - vii) or mixtures thereof;
- f) and mixtures thereof; and

the index n is an integer from 1 to 3.

The fragrance delivery systems of the present invention which comprise a heterocyclic pro-fragrance or pro-accord comprise:

- A) from about 1%, preferably from about 10%, more preferably from about 25% to about 100%, preferably to about 90%, more preferably to about 75%, most preferably to about 50% by weight, of a pro-fragrance and/or pro-accord component; and
- B) optionally from about 1%, preferably from about 25% to about 99%, preferably to about 90%, more preferably to about 75%, most preferably to about 50% by weight, of a fragrance raw material component.

The present invention further relates to a method for providing an sustained duration aesthetic perfume or fragrance benefit comprising the step of contacting a surface with a composition which comprises the fragrance delivery system of the present invention.

The present invention further relates to pro-fragrance libraries which are formed from an admixture of two or more fragrance raw materials and which use the same heterocyclic ring to provide a releasable admixture of fragrance ingredients suitable for use in the fragrance delivery systems of the present invention.

These and other objects, features and advantages will become apparent to those of ordinary skill in the art from a reading of the following detailed description and the appended claims. All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius ($^{\circ}$ C) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to pro-fragrances and/or pro-accords which release an aldehyde or ketone fragrance raw material. The present invention further relates to fragrance delivery systems which comprise one or more of the herein described pro-fragrances.

Key to the pro-fragrances and/or pro-accords of the present invention is the ability of the formulator to prepare a compound (pro-fragrance or pro-accord) which has a specific release rate of aldehyde or ketone. The formulator may design pro-fragrances or pro-accords to release at any rate which the formulator finds useful to the consumer. In addition, by determining the Fragrance Release Half-life of each particular pro-fragrance, the formulator is able to make a side by side comparison of structurally dissimilar molecules and evaluate their relative fragrance raw material release patterns. In this way not only can the formulator determine with minimal

experimentation whether a compound is suitable for use as a pro-fragrance, but also determine the release profile of the molecule. Therefore, a slight structural modification can result in a more finely tuned fragrance delivery system.

Mixtures of fragrance materials are known by those skilled in the art of fragrances and perfumes as "accords". The term "accord" as used herein is defined as "a mixture of two or more 'fragrance raw materials' which are artfully combined to impart a pleasurable scent, odor, essence, or fragrance characteristic". For the purposes of the present invention "fragrance raw materials" are herein defined as compounds having a molecular weight of at least 100 g/mol and which are useful in imparting an odor, fragrance, essence, or scent either alone or in combination with other "fragrance raw materials".

The fragrance delivery systems of the present invention comprise one or more of the herein described pro-fragrances or pro-accords. In its broadest form, the fragrance delivery system comprises:

- A) from about 1%, preferably from about 10%, more preferably from about 25% to about 100%, preferably to about 90%, more preferably to about 75%, most preferably to about 50% by weight, of a cyclic pro-fragrance or pro-accord component as described herein below; and
- B) optionally from about 1%, preferably from about 25% to about 99%, preferably to about 90%, more preferably to about 75%, most preferably to about 50% by weight, of a fragrance raw material component.

The fragrance delivery system of the present invention is therefore an admixture of pro-fragrances/pro-accords and optionally other fragrance raw materials which provides a sustained and enhanced delivery of fragrance or other aesthetic perfume benefit to the user. The fragrance delivery system of the present invention can be used in any composition which intends to provide an aesthetic benefit *inter alia* fine fragrances, perfumes, personal care products, deodorants, shampoos, laundry detergents, malodor masking agents.

Aesthetic perfume or fragrance raw material delivery systems typically comprise components which react with human olfactory sites resulting in what is known as a "fragrance". Typical molecules which comprise perfume fragrances are linear and cyclic alkenes (i.e., terpenes), primary, secondary and tertiary alcohols, nitriles, ethers, saturated and unsaturated aldehydes, esters, ketones, and mixtures thereof. Each of these perfume fragrances can be classified according to its volatility into one of three categories: "top note", "middle note", and "base note".

For the purposes of the present invention "top note" fragrances are defined as "fragrances having a high vapor pressure, and when applied to a paper sachet, vaporization takes place within 2 hours, and no scent remains; essentially, the initial impression of the perfume formulation is provided by top notes".

For the purposes of the present invention "middle note" fragrances are defined as "fragrances having a medium vapor pressure, and when applied to a paper sachet, the scent remains from about 2 to about 6 hours; essentially, middle notes provide the skeleton of the perfume formulation".

For the purposes of the present invention "base note" fragrances are defined as "fragrances having a low vapor pressure and high retentivity, and when applied to a paper sachet, the scent remains for more than about 6 hours; essentially, base notes provide the characteristic of the perfume formulation.

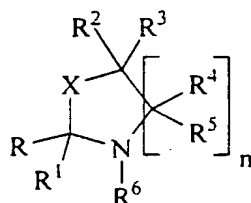
The terms "top note", "middle note", and "base note" are well recognized by those skilled in the art of fragrance-containing compositions. However, reference to a specific fragrance raw material as a "top note" within the present invention does mean that others skilled in the art of fragrance-containing compositions may not categorize the same ingredient as a "middle note". The same applies to fragrance raw materials referred to as "middle notes" and "base notes".

Typically "fragrance raw materials" comprise *inter alia* alcohols, ketones, aldehydes, esters, ethers, nitriles, and alkenes such as terpenes. A listing of common "fragrance raw materials" can be found in various reference sources, for example, "Perfume and Flavor Chemicals", Vols. I and II: Steffen Arctander Allured Pub. Co. (1994) and "Perfumes: Art, Science and Technology"; Müller, P. M. and Lamparsky, D., Blackie Academic and Professional (1994) both incorporated herein by reference.

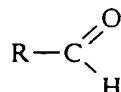
Aldehyde and Ketone Releasing Pro-fragrances

The fragrance delivery systems of the present invention comprise one or more heterocyclic aldehyde-releasing and/or ketone-releasing pro-fragrances, preferably oxazolidines, tetrahydro-1,3-oxazines, thiazolidines, or tetrahydro-1,3-thiazines, more preferably oxazolidines, or tetrahydro-1,3-oxazines, most preferably oxazolidines.

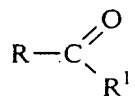
The pro-fragrances or pro-accords which are suitable for use in the fragrance delivery systems described herein have the formula:



and are capable of releasing an aldehyde fragrance raw material having the formula:



or a ketone fragrance raw material having the formula:



For the purposes of the fragrance delivery systems which comprise one or more heterocyclic pro-fragrances or pro-accords, R units are defined herein as:

- a) C₆-C₂₂, preferably C₆-C₁₈, more preferably C₆-C₁₅ substituted or unsubstituted linear alkyl; one or more examples of a fragrance raw material which comprises this unit includes nonanal and decanal;
- b) C₆-C₂₂, preferably C₆-C₁₈, more preferably C₆-C₁₅ substituted or unsubstituted branched alkyl; one or more examples of a fragrance raw material which comprises this unit includes 2-methyldecanal;
- c) C₆-C₂₂, preferably C₆-C₁₈, more preferably C₆-C₁₅ substituted or unsubstituted linear alkenyl; one or more examples of a fragrance raw material which comprises this unit includes 10-undecenal;
- d) C₆-C₂₂, preferably C₆-C₁₈, more preferably C₆-C₁₅ substituted or unsubstituted branched alkenyl; one or more examples of a fragrance raw material which comprises this unit includes citral, melonal, and neral;
- e) C₆-C₂₂, preferably C₆-C₁₈, more preferably C₆-C₁₀ substituted or unsubstituted cycloalkyl; one or more examples of a fragrance raw material which comprises this unit includes cyclopentadecanone;
- f) C₆-C₂₂, preferably C₆-C₁₅, more preferably C₆-C₁₅ substituted or unsubstituted branched cycloalkyl; one or more examples of a fragrance raw material which comprises this unit includes camphor and muscone;

- g) C₆-C₂₂, preferably C₆-C₁₈, more preferably C₆-C₁₅ substituted or unsubstituted cycloalkenyl; one or more examples of a fragrance raw material which comprises this unit includes civetone;
- h) C₆-C₂₂, preferably C₆-C₁₈, more preferably C₆-C₁₅ substituted or unsubstituted branched cycloalkenyl; one or more examples of a fragrance raw material which comprises this unit includes α -damascone and β -ionone;
- i) C₆-C₂₂, preferably C₆-C₁₈, more preferably C₆-C₁₀ substituted or unsubstituted aryl wherein said aryl unit preferably comprises a phenyl unit; one or more examples of a fragrance raw material which comprises this unit includes benzaldehyde, hydrotropaldehyde and vanillin;
- j) C₆-C₂₂, preferably C₆-C₁₅, more preferably C₆-C₁₅ substituted or unsubstituted heterocyclicalkyl;
- k) C₆-C₂₂, preferably C₆-C₁₈, more preferably C₆-C₁₅ substituted or unsubstituted heterocyclicalkenyl; one or more examples of a fragrance raw material which comprises this unit includes;
- l) and mixtures thereof;

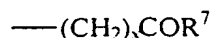
R¹ is:

- a) hydrogen;
- b) C₁-C₁₀, preferably C₁-C₅ substituted or unsubstituted linear alkyl;
- c) C₃-C₁₀, preferably C₃-C₅ substituted or unsubstituted branched alkyl;
- d) C₂-C₁₀, preferably C₂-C₅ substituted or unsubstituted linear alkenyl;
- e) C₃-C₁₀, preferably C₄-C₁₀ substituted or unsubstituted branched alkenyl;
- f) C₃-C₁₅, preferably C₆-C₁₀ substituted or unsubstituted cycloalkyl;
- g) C₄-C₁₅, preferably C₆-C₁₀ substituted or unsubstituted branched cycloalkyl;
- h) C₄-C₁₅, preferably C₆-C₁₀ substituted or unsubstituted cycloalkenyl;
- i) C₅-C₁₅, preferably C₆-C₁₀ substituted or unsubstituted branched cycloalkenyl;
- j) C₆-C₁₅, preferably C₆-C₁₀ substituted or unsubstituted aryl;
- k) C₆-C₂₂, preferably C₆-C₁₀ substituted or unsubstituted heterocyclicalkyl;
- l) C₆-C₂₂, preferably C₆-C₁₀ substituted or unsubstituted heterocyclicalkenyl;

R and R¹ can be taken together to form a substituted or unsubstituted ring having in the ring from 3 to 10 carbon atoms: one or more examples of which are substituted cyclopentanone derivatives inter alia hedione and nectaryl; and

each R², R³, R⁶ and each R⁴ and R⁵ pair are independently:

- a) R^1 ;
- b) hydroxyl;
- c) a carbonyl comprising unit having the formula:



wherein R^7 is:

- i) -OH, in the case of carboxylic acids;
- ii) $-OR^8$, in the case of esters wherein R^8 is hydrogen; C_1-C_{15} , preferably C_1-C_{10} , more preferably C_1-C_4 substituted or unsubstituted linear alkyl; C_3-C_{15} , preferably C_3-C_{10} , more preferably C_3-C_4 substituted or unsubstituted branched alkyl; C_2-C_{22} , preferably C_2-C_{10} , more preferably C_2-C_4 substituted or unsubstituted linear alkenyl; C_3-C_{22} substituted or unsubstituted branched alkenyl, or mixtures thereof;
- iii) $-N(R^9)_2$ in the case of amides wherein each R^9 is independently hydrogen; C_1-C_{15} , preferably C_1-C_{10} , more preferably C_1-C_4 substituted or unsubstituted linear alkyl; C_3-C_{15} , preferably C_3-C_{10} , more preferably C_3-C_4 substituted or unsubstituted branched alkyl; or mixtures thereof;
- iv) C_1-C_{22} , preferably C_1-C_5 substituted or unsubstituted linear alkyl;
- v) C_1-C_{22} , preferably C_3-C_5 substituted or unsubstituted branched alkyl;
- vi) C_2-C_{22} , preferably C_2-C_5 substituted or unsubstituted linear alkenyl;
- vii) C_3-C_{22} , preferably C_4-C_{10} substituted or unsubstituted branched alkenyl;
- viii) C_5-C_{22} , preferably C_6-C_{10} substituted or unsubstituted cycloalkyl;
- ix) C_6-C_{22} , preferably C_6-C_{10} substituted or unsubstituted aryl;
- x) C_6-C_{22} , preferably C_6-C_{10} substituted or unsubstituted heterocyclicalkyl;
- xi) C_6-C_{22} , preferably C_6-C_{10} substituted or unsubstituted heterocyclicalkenyl;

the index is from 0 to 22;

- e) alkyleneoxy units having the formula:



wherein each R^{10} , R^{11} , and R^{12} is independently;

- i) hydrogen;
- ii) -OH;
- iii) C_1-C_4 alkyl, preferably methyl;
- iv) or mixtures thereof; preferably R^{10} , R^{11} , and R^{12} are each hydrogen;

R¹³ is:

- i) hydrogen;
- ii) C₁-C₄ alkyl, preferably methyl;
- iii) or mixtures thereof; preferably R¹³ is methyl or hydrogen, more preferably hydrogen;

R¹⁴ is:

- i) hydrogen;
- ii) C₁-C₄ alkyl, preferably methyl;
- iii) or mixtures thereof; preferred R¹⁴ is hydrogen;

R¹⁰ and R¹¹ can be taken together to form a C₃-C₆ spiroannulated ring, carbonyl unit, or mixtures thereof; y has the value from 0 to 10, z has the value from 1 to 50;

- f) any two R², R³, R⁴, R⁵, or R⁶ units can be taken together, and where feasible, combined to form:
 - i) a carbonyl moiety;
 - ii) a C₃-C₆ spiroannulated ring;
 - iii) a heterocyclic aromatic ring comprising from 5 to 7 atoms;
 - iv) a non-heterocyclic aromatic ring comprising from 5 to 7 atoms;
 - v) a heterocyclic ring comprising from 5 to 7 atoms;
 - vi) a non-heterocyclic ring comprising from 5 to 7 atoms;
 - vii) or mixtures thereof;
- g) and mixtures thereof;

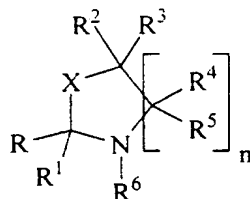
the index n is an integer from 1 to 3, preferably 1 or 2, more preferably 1.

For the purposes of the present invention, the term "substituted" is defined herein as "compatible moieties which replace a hydrogen atom". For the purposes of the present invention, hydrogens which are substitutable are labeled as R' units in the following examples. Non-limiting examples of substituents which can replace hydrogen atoms are C₁-C₂₂ linear or branched hydrocarbyl units *inter alia* alkyl, alkenyl; hydroxy, nitrilo, nitro, carboxyl (-CHO; -CO₂H; -CO₂R"; -CONH₂; -CONHR"; -CONR""₂; wherein R" is C₁-C₁₂ linear or branched alkyl), amino, C₁-C₁₂ mono- and dialkylamino, and mixtures thereof. However, the formulator may wish to include other substituents not specifically mentioned herein. Not each hydrogen of a substituted unit, i.e., substituted linear alkyl, must be substituted; only one hydrogen must be

substituted by another moiety for a unit to be "substituted" for the purposes of the present invention.

However, more than one definition may apply to a unit which is suitable for use in the pro-fragrances of the present invention. For example, as defined herein above, R may be a C₆-C₂₂ substituted or unsubstituted, linear or branched alkyl moiety. The unit 3-propylheptyl, which comprises 10 carbon atoms may be considered a C₁₀ branched alkyl unit or a C₇ linear alkyl unit having a hydrogen atom substituted by a C₃ alkyl unit. Either definition applies equally well for the purposes of the present invention.

The present invention further relates to heterocyclic pro-fragrances, preferably oxazolidines and tetrahydro-1,3-oxazines, having the formula:



wherein said pro-fragrance or pro-accord releases an aldehyde or a ketone fragrance raw material, wherein X is oxygen or sulfur; R is:

- a) C₆-C₂₂ substituted or unsubstituted linear alkyl;
- b) C₆-C₂₂ substituted or unsubstituted branched alkyl;
- c) C₆-C₂₂ substituted or unsubstituted linear alkenyl;
- d) C₆-C₂₂ substituted or unsubstituted branched alkenyl;
- e) C₆-C₂₂ substituted or unsubstituted cycloalkyl;
- f) C₆-C₂₂ substituted or unsubstituted branched cycloalkyl;
- g) C₆-C₂₂ substituted or unsubstituted cycloalkenyl;
- h) C₆-C₂₂ substituted or unsubstituted branched cycloalkenyl;
- i) C₆-C₂₂ substituted or unsubstituted aryl;
- j) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- k) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;
- l) and mixtures thereof.

R¹ is:

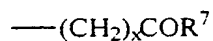
- a) hydrogen;
- b) C₁-C₁₀ substituted or unsubstituted linear alkyl;
- c) C₃-C₁₀ substituted or unsubstituted branched alkyl;

- d) C₂-C₁₀ substituted or unsubstituted linear alkenyl;
- e) C₃-C₁₀ substituted or unsubstituted branched alkenyl;
- f) C₄-C₁₅ substituted or unsubstituted cycloalkyl;
- g) C₄-C₁₅ substituted or unsubstituted branched cycloalkyl;
- h) C₅-C₁₅ substituted or unsubstituted cycloalkenyl;
- i) C₅-C₁₅ substituted or unsubstituted branched cycloalkenyl;
- j) C₆-C₁₅ substituted or unsubstituted aryl;
- k) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- l) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;
- m) and mixtures thereof;

R and R¹ can be taken together to form a substituted or unsubstituted ring having in the ring from 3 to 10 carbon atoms;

each R², R³, and each R⁴ and R⁵ pair are independently:

- a) R¹;
- b) hydroxyl;
- c) a carbonyl comprising unit having the formula:



wherein R⁷ is:

- i) -OH;
- ii) -OR⁸ wherein R⁸ is hydrogen, C₁-C₁₅ substituted or unsubstituted linear alkyl, C₁-C₁₅ substituted or unsubstituted branched alkyl, C₂-C₂₂ substituted or unsubstituted linear alkenyl, C₃-C₂₂ substituted or unsubstituted branched alkenyl, or mixtures thereof, wherein said substitution is not halogen;
- iii) -N(R⁹)₂ wherein R⁹ is hydrogen, C₁-C₆ substituted or unsubstituted linear alkyl, C₃-C₆ substituted or unsubstituted branched alkyl, or mixtures thereof;
- iv) C₁-C₂₂ substituted or unsubstituted linear alkyl;
- v) C₁-C₂₂ substituted or unsubstituted branched alkyl;
- vi) C₂-C₂₂ substituted or unsubstituted linear alkenyl;
- vii) C₃-C₂₂ substituted or unsubstituted branched alkenyl;
- viii) C₅-C₂₂ substituted or unsubstituted cycloalkyl;
- ix) C₆-C₂₂ substituted or unsubstituted aryl;

- x) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
 - xi) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;
- the index x is from 0 to 22;

- d) alkyleneoxy units having the formula:



wherein each R¹⁰, R¹¹, and R¹² is independently;

- i) hydrogen;
- ii) -OH;
- iii) C₁-C₄ alkyl;
- iv) or mixtures thereof;

R¹³ is:

- i) hydrogen;
- ii) C₁-C₄ alkyl;
- iii) or mixtures thereof;

R¹⁴ is:

- i) hydrogen;
- ii) C₁-C₄ alkyl;
- iii) or mixtures thereof;

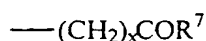
R¹⁰ and R¹¹ can be taken together to form a C₃-C₆ spiroannulated ring, carbonyl unit, or mixtures thereof; y has the value from 0 to 10, z has the value from 1 to 50;

- e) and mixtures thereof:

R⁶ is:

- a) C₁-C₁₀ substituted linear alkyl;
- b) C₃-C₁₀ substituted branched alkyl;
- c) C₂-C₁₀ substituted or unsubstituted linear alkenyl;
- d) C₃-C₁₀ substituted or unsubstituted branched alkenyl;
- e) C₃-C₁₅ substituted cycloalkyl;
- f) C₄-C₁₅ substituted or unsubstituted branched cycloalkyl;
- g) C₄-C₁₅ substituted or unsubstituted cycloalkenyl;
- h) C₅-C₁₅ substituted or unsubstituted branched cycloalkenyl;
- i) C₆-C₁₅ substituted aryl;
- j) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;

- k) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;
 l) a carbonyl comprising unit having the formula:



wherein R⁷ is:

- i) -OH;
- ii) -OR⁸ wherein R⁸ is hydrogen, C₁-C₁₅ substituted linear alkyl, C₁₁-C₁₅ unsubstituted linear alkyl, C₁-C₁₅ substituted branched alkyl, C₁₁-C₁₅ unsubstituted branched alkyl, C₂-C₂₂ substituted or unsubstituted linear alkenyl, C₃-C₂₂ substituted or unsubstituted branched alkenyl, or mixtures thereof, wherein said substitution is not halogen or thioalkyl;
- iii) -N(R⁹)₂ wherein R⁹ is hydrogen, C₁-C₆ substituted or unsubstituted linear alkyl, C₃-C₆ substituted or unsubstituted branched alkyl, or mixtures thereof;
- iv) C₁-C₂₂ substituted or unsubstituted linear alkyl;
- v) C₁-C₂₂ substituted or unsubstituted branched alkyl;
- vi) C₂-C₂₂ substituted or unsubstituted linear alkenyl;
- vii) C₃-C₂₂ substituted or unsubstituted branched alkenyl;
- viii) C₅-C₂₂ substituted or unsubstituted cycloalkyl;
- ix) C₆-C₂₂ substituted or unsubstituted aryl;
- x) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- xi) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;

the index x is from 0 to 22;

- m) alkyleneoxy units having the formula:



wherein each R¹⁰, R¹¹, and R¹² is independently:

- i) hydrogen;
- ii) -OH;
- iii) C₁-C₄ alkyl;
- iv) or mixtures thereof;

R¹³ is:

- i) hydrogen;
- ii) C₁-C₄ alkyl;
- iii) or mixtures thereof;

R^{14} is:

- i) hydrogen;
- ii) C_1 - C_4 alkyl;
- iii) or mixtures thereof;

R^{10} and R^{11} can be taken together to form a C_3 - C_6 spiroannulated ring, carbonyl unit, or mixtures thereof; y has the value from 0 to 10, z has the value from 1 to 50;

- n) and mixtures thereof;

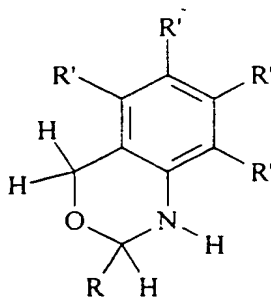
any two R^2 , R^3 , R^4 , R^5 , or R^6 units can be taken together to form:

- i) a carbonyl moiety;
- ii) a C_3 - C_6 spiroannulated ring;
- iii) a heterocyclic aromatic ring comprising from 5 to 7 atoms;
- iv) a non-heterocyclic aromatic ring comprising from 5 to 7 atoms;
- v) a heterocyclic ring comprising from 5 to 7 atoms;
- vi) a non-heterocyclic ring comprising from 5 to 7 atoms;
- vii) or mixtures thereof; and

the index n is an integer from 1 to 3.

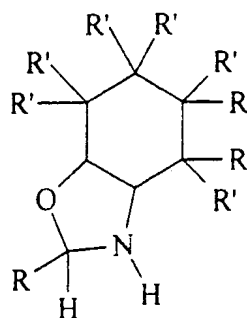
The pro-fragrance compounds of the present invention do not comprise a halogen nor does the R^6 unit comprise a thioalkyl moiety.

A non-limiting example of an aldehyde-releasing pro-fragrance suitable for use in the fragrance delivery systems according to the present invention is 1,3-oxazine having the formula:



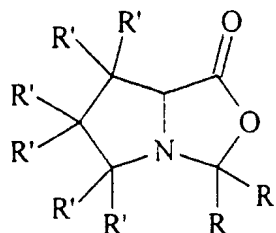
wherein R^1 , R^2 , R^3 and R^6 are each hydrogen; n is equal to 2, therefore the pro-fragrance comprises two sets of R^4 and R^5 units, and wherein further the first pair of R^4 and R^5 units are taken together with the second pair of R^4 and R^5 units to form a fused aromatic ring having 6 carbon atoms. R' indicates substitutable hydrogens.

wherein further non-limiting example of a fragrance suitable for use in the fragrance delivery systems according to the present invention is the oxazolidine having the formula:



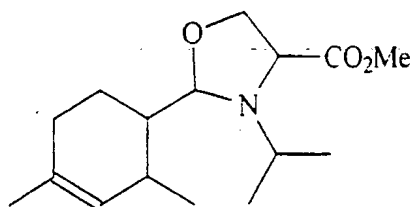
wherein R^1 and R^6 are each hydrogen; n is equal to 1. R^3 and R^5 are each hydrogen, and the R^2 unit is taken together with the R^4 unit to form a substituted cycloalkyl ring having 6 carbon atoms, wherein further R' indicates substitutable hydrogens.

A non-limiting example of a ketone-releasing pro-fragrance suitable for use in the fragrance delivery systems according to the present invention is the fused ring compound having the formula:



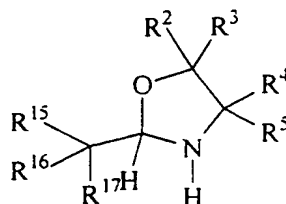
wherein n is equal to 1, R^4 is equal to hydrogen, R^2 and R^3 are taken together to form a carbonyl unit, and the R^5 unit is taken together with the R^6 unit to form a substituted cycloalkyl ring having 5 atoms, wherein further R' indicates substitutable hydrogens.

An example of a preferred heterocyclic pro-fragrance according to the present invention is 2-(2,4-dimethylcyclohex-3-enyl)-5-carboxymethyl-N-isopropyl-1,3-oxazolidine having the formula:



which is obtained from the reaction of N-isopropyl serine methyl ester and triplal.

One class of preferred pro-fragrances of the present invention are the tertiary α -carbon 1,3-oxazolidines having the formula:

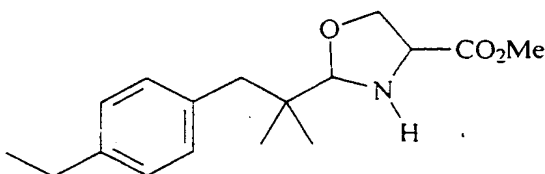


wherein R^2 , R^3 , R^4 , and R^5 is the same as defined herein above, R^{15} , R^{16} , and R^{17} are each independently:

- a) C_1 - C_{22} substituted or unsubstituted linear alkyl, preferably methyl or ethyl, more preferably methyl;
- b) C_3 - C_{22} substituted or unsubstituted branched alkyl;
- c) C_2 - C_{22} substituted or unsubstituted linear alkenyl;
- d) C_3 - C_{22} substituted or unsubstituted branched alkenyl;
- e) C_3 - C_{22} substituted or unsubstituted cycloalkyl;
- f) C_4 - C_{22} substituted or unsubstituted branched cycloalkyl;
- g) C_4 - C_{22} substituted or unsubstituted cycloalkenyl;
- h) C_4 - C_{22} substituted or unsubstituted branched cycloalkenyl;
- i) C_6 - C_{22} substituted or unsubstituted aryl;
- j) C_6 - C_{22} substituted or unsubstituted heterocyclicalkyl;
- k) C_6 - C_{22} substituted or unsubstituted heterocyclicalkenyl;
- l) any two R^{15} , R^{16} , and R^{17} units can be taken together to form a substituted or unsubstituted ring having from 3-10 carbon atoms;
- m) and mixtures thereof;

Preferably one R^{15} , R^{16} , or R^{17} unit, more preferably two R^{15} , R^{16} , or R^{17} unit is methyl.

A non-limiting example of an α -carbon tertiary 1,3-oxazolidine pro-fragrance has the formula:



wherein said pro-fragrance is formed from serine methyl ester and florhydral.

Non-limiting examples of aldehydes which can be suitably released by the pro-fragrances of the present invention include phenylacetaldehyde, p-methyl phenylacetaldehyde, p-isopropyl phenylacetaldehyde, methylnonyl acetaldehyde, phenylpropanal, 3-(4-*t*-butylphenyl)-2-methyl propanal (Lilial), 3-(4-*t*-butylphenyl)-propanal (Bourgeonal), 3-(4-

methoxyphenyl)-2-methylpropanal (Canthoxal), 3-(4-isopropylphenyl)-2-methylpropanal (Cymal), 3-(3,4-methylenedioxyphenyl)-2-methylpropanal (Helional), 3-(4-ethylphenyl)-2,2-dimethylpropanal (Floralozone), phenylbutanal, 3-methyl-5-phenylpentanal, hexanal, *trans*-2-hexenal, *cis*-hex-3-enal, heptanal, *cis*-4-heptenal, 2-ethyl-2-heptenal, 2,6-dimethyl-5-heptenal (Melonal), 2,4-heptadienal, octanal, 2-octenal, 3,7-dimethyloctanal, 3,7-dimethyl-2,6-octadien-1-al, 3,7-dimethyl-1,6-octadien-3-al, 3,7-dimethyl-6-octenal (citronellal), 3,7-dimethyl-7-hydroxyoctan-1-al (hydroxy citronellal), nonanal, 6-nonenal, 2,4-nonadienal, 2,6-nonadienal, decanal, 2-methyl decanal, 4-decenal, 9-decenal, 2,4-decadienal, undecanal, 2-methyldecanal, 2-methylundecanal, 2,6,10-trimethyl-9-undecenal (Adoxal), undec-10-enyl aldehyde, undec-8-enanal, dodecanal, tridecanal, tetradecanal, anisaldehyde, bourgenonal, cinnamic aldehyde, α -amylcinnam-aldehyde, α -hexyl cinnamaldehyde, methoxy-cinnamaldehyde, isocyclocitral, citronellyl oxyacet-aldehyde, cortexaldehyde, cumminic aldehyde, cyclamen aldehyde, florhydral, heliotropin, hydrotropic aldehyde, vanillin, ethyl vanillin, benzaldehyde, *p*-methyl benzaldehyde, 3,4-dimethoxybenzaldehyde, 3- and 4-(4-hydroxy-4-methyl-pentyl)-3-cyclohexene-1-carboxaldehyde (Lyrall), 2,4-dimethyl-3-cyclohexene-1-carboxaldehyde (Triplal), 1-methyl-3-(4-methylpentyl)-3-cyclohexencarboxaldehyde (Vernaldehyde), *p*-methylphenoxyacetaldehyde (Xi aldehyde), and mixtures thereof.

Non-limiting examples of ketones which can be suitably released by the pro-fragrances of the present invention include α -damascone, β -damascone, δ -damascone, β -damascenone, muscone, 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone (cashmeran), *cis*-jasmone, dihydrojasmone, α -ionone, β -ionone, dihydro- β -ionone, γ -methyl ionone, α -*iso*-methyl ionone, 4-(3,4-methylenedioxyphenyl)butan-2-one, 4-(4-hydroxyphenyl)butan-2-one, methyl β -naphthyl ketone, methyl cedryl ketone, 6-acetyl-1,1,2,4,4,7-hexamethyltetralin (tonalid), *l*-carvone, 5-cyclohexadecen-1-one, acetophenone, decatone, 2-[2-(4-methyl-3-cyclohexenyl-1-yl)propyl]cyclopentan-2-one, 2-*sec*-butylcyclohexanone, β -dihydro ionone, allyl ionone, α -irone, α -cetone, α -irisone, acetanisole, geranyl acetone, 1-(2-methyl-5-isopropyl-2-cyclohexenyl)-1-propanone, acetyl diisoamylene, methyl cyclocitronone, 4-*t*-pentyl cyclohexanone, *p*-*t*-butylcyclohexanone, *o*-*t*-butylcyclohexanone, ethyl amyl ketone, ethyl pentyl ketone, menthone, methyl-7,3-dihydro-2H-1,5-benzodioxepine-3-one, fenchone, and mixtures thereof.

Fragrance Delivery System

The present invention further relates to fragrance delivery systems which are suitable for use in delivering an enhanced duration aesthetic benefit. The fragrance delivery systems are

suitable for use and are compatible with any composition which may require a fragrance *inter alia* fine fragrances, perfumes, personal care products, deodorants, shampoos, laundry detergents, malodor masking agents.

In general, the compositions of the present invention, other than fine fragrances or perfumes which are described herein below, comprise from about 0.01%, preferably from about 0.05%, more preferably from about 0.1%, most preferably from about 0.5% to about 10%, preferably to about 7%, more preferably to about 5%, most preferably to about 3% by weight, of a fragrance delivery system comprising:

- A) from about 1%, preferably from about 10%, more preferably from about 25% to about 100%, preferably to about 90%, more preferably to about 75%, most preferably to about 50% by weight, of a pro-fragrance component comprising:
 - i) at least 1% by weight (10 ppb of the composition which employs the fragrance delivery system), of an aldehyde or ketone releasing pro-fragrance component according to the present invention as described herein;
 - ii) optionally at least 1% by weight (10 ppb of the composition which employs the fragrance delivery system), of one or more pro-accords formed from at least one fragrance raw material, wherein said pro-accord is selected from the group consisting of acetals, ketals, orthoesters, orthocarbonates, and mixtures thereof, each pro-accord releasing upon hydrolysis said fragrance raw material from which it is formed, said fragrance raw materials selected from the group consisting of primary, secondary, and tertiary alcohols, aldehydes, ketones, esters, carbonates, and mixtures thereof, provided each pro-accord:
 - a) is formed from at least one fragrance raw material having a molecular weight greater than or equal to about 100 g/mol;
 - b) has a fragrance release half-life of greater than or equal to about 0.1 hours at pH 5.3 and less than or equal to about 12 hours at pH 2.5 when measured in NaH_2PO_4 buffer;
 - iii) the balance carriers, stabilizers, and other adjunct ingredients; and
- B) optionally from about 1%, preferably from about 25% to about 99%, preferably to about 90%, more preferably to about 75%, most preferably to about 50% by weight, a fragrance raw material component comprising:

- i) optionally at least 1% by weight, of a mixture of one or more base note fragrances;
- ii) optionally at least 1% by weight, of a mixture of one or more top or middle note fragrances;
- ii) optionally the balance carriers, fixatives, and other adjunct ingredients.

However, some compositions according to the present invention are fine fragrances or perfumes. These embodiments typically comprise only fragrance raw materials, pro-fragrances, pro-accords, carriers, and stabilizers. The fine fragrance and perfume compositions which utilize the cyclic pro-fragrances of the present invention comprise:

- a) at least 0.01%, preferably from about 0.1%, more preferably from about 5%, most preferably from about 20% to about 100%, preferably to about 75%, more preferably to 50% by weight, of an aldehyde or ketone releasing pro-fragrance component according to the present invention;
- b) optionally from about 1%, preferably from about 25% to about 99.99%, preferably to about 99.9%, more preferably to about 95%, most preferably to about 50% by weight, of one or more pro-accords which comprise n fragrance raw materials but which release $n+1$ fragrance raw materials, preferably orthoesters, orthocarbonates, β -ketoesters, and mixtures thereof;
- c) optionally from about 1%, preferably from about 25% to about 99.99%, preferably to about 99.9%, more preferably to about 95%, most preferably to about 50% by weight, of one or more pro-fragrances selected from the group consisting of acetals, ketals, orthoesters, orthocarbonate, ortholactones, β -ketoesters, and mixtures thereof;
- d) optionally from about 1%, preferably from about 25% to about 99.99%, preferably to about 99.9%, more preferably to about 95%, most preferably to about 50% by weight, of one or more fragrance raw materials, preferably one or more fragrance raw materials which are released by a pro-fragrance or pro-accord which comprises the fragrance delivery system; and
- e) optionally one or more carriers, fixatives, stabilizers, or adjunct ingredients.

When present, the carriers, fixatives, or stabilizers will comprise the balance of the compositions. Typical carriers are methanol, ethanol (preferred), iso-propanol, polyethylene glycol, as well as water in some instances, especially as a vehicle to deliver materials which provide reserve alkalinity to the fragrance delivery system. Fixatives serve to lower the

volatility of certain top and middle notes in order to extend their contact time on skin. Adjunct ingredients include perfume raw material components which are essential oils and are therefore not a single chemical entity. In addition, the adjunct ingredients may be mixtures of materials which serve a purpose in addition to providing a pleasurable odor (i.e., an astringent in a personal hygiene article).

For the purposes of the fragrance delivery systems of the present invention, a "pro-accord which comprises n fragrance raw materials but which releases $n+1$ fragrance raw materials" is defined as "a compound which is prepared from one or more fragrance raw materials, said fragrance raw material being chemically transformed into a "releasable form" such that when said releasable form breaks down, the original fragrance raw material is released as well as at least one other fragrance raw material which was not a starting material used in forming the releasable form". The term "releasable form" is defined herein as a "pro-fragrance or pro-accord compound, which ever form is applicable". Non-limiting examples of "releasable forms" or pro-accords which satisfy the $n + 1$ requirement are as follows.

The pro-accord tris(9-decenyl) orthoformate is prepared by treating 9-decenol (i.e., Rosalva), which is a fragrance raw material as defined herein, with a suitable amount of triethyl orthoformate, not a fragrance raw material as defined herein, in the presence of an acid catalyst optionally in the presence of a solvent. Tris(9-decenyl) when exposed to suitable conditions (e.g., exposure to the acid mantle of human skin) breaks down to release a mixture of 9-decenol and 9-decenyl formate, both of which are fragrance raw materials. Therefore, one fragrance raw material is used to prepare a releasable form (pro-accord) of two fragrance raw materials.

The pro-accord 3,7-dimethyl-1,6-octadien-3-yl 3-(β -naphthyl)-3-oxo-propionate, which is a β -ketoester pro-accord, is prepared by treating 3,7-dimethyl-1,6-octadien-3-ol (linalool), which is a fragrance raw material according to the present invention, with diketene under suitable conditions to form intermediate 3,7-dimethyl-1,6-octadien-3-yl 3-oxo-butyrate, which is subsequently treated with 2-naphthoyl chloride to yield the pro-accord. 3,7-Dimethyl-1,6-octadien-3-yl 3-(β -naphthyl)-3-oxo-propionate when exposed to suitable conditions (e.g., exposure to nascent moisture) breaks down to release a mixture of linalool and methyl β -naphthyl ketone, both of which are fragrance raw materials as defined herein.

As described herein above, an optional component of the fragrance delivery systems of the present invention are pro-fragrances or pro-accords which are not heterocyclic aldehyde and/or ketone releasing pro-fragrances. The optional pro-accords or pro-fragrances are equally

functional in either personal care compositions *inter alia* lotions, creams, deodorants or personal fragrance compositions *inter alia* fine fragrances, perfumes.

Preferred optional pro-accords and/or pro-fragrances include, but are not limited to, orthoesters, orthocarbonates, acetals, ketals, ortholactones, and β -ketoesters.

Non-limiting examples of optional orthoesters which are suitable for use in the fragrance delivery systems of the present invention include tris-geranyl orthoformate, tris(*cis*-3-hexen-1-yl) orthoformate, tris(phenylethyl) orthoformate, bis(citronellyl) ethyl orthoacetate, tris(citronellyl) orthoformate, tris(*cis*-6-nonenyl) orthoformate, tris(phenoxyethyl) orthoformate, tris(geranyl, neryl) orthoformate (70:30 geranyl:neryl), tris(9-decenyl) orthoformate, tris(3-methyl-5-phenylpentanyl) orthoformate, tris(6-methylheptan-2-yl) orthoformate, tris([4-(2,2,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-yl] orthoformate, tris[3-methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-yl] orthoformate, trismenthyl orthoformate, tris(4-isopropylcyclohexylethyl-2-yl) orthoformate, tris-(6,8-dimethylnonan-2-yl) orthoformate, tris-phenylethyl orthoacetate, tris(*cis*-3-hexen-1-yl) orthoacetate, tris(*cis*-6-nonenyl) orthoacetate, tris-citronellyl orthoacetate, bis(geranyl) benzyl orthoacetate, tris(geranyl) orthoacetate, tris(4-isopropylcyclohexylmethyl) orthoacetate, tris(benzyl) orthoacetate, tris(2,6-dimethyl-5-heptenyl) orthoacetate, bis(*cis*-3-hexen-1-yl) amyl orthoacetate, and neryl citronellyl ethyl orthobutyrate.

Non-limiting examples of optional orthocarbonates which are suitable for use in the fragrance delivery systems of the present invention include bis(ethyl) bis(geranyl) orthocarbonate, bis(ethyl) bis(phenylethyl) orthocarbonate, bis(ethyl) bis(*cis*-3-hexenyl) orthocarbonate, bis(ethyl) bis(citronellyl) orthocarbonate, bis(ethyl) bis(linalyl) orthocarbonate, bis(ethyl) bis(menthyl) orthocarbonate, bis(dodecyl) bis(geranyl) orthocarbonate, and bis(dodecyl) bis(phenylethyl) orthocarbonate.

Non-limiting examples of optional acetals which are suitable for use in the fragrance delivery systems of the present invention include bis(*cis*-3-hexenyl) vanillin, bis(geranyl) cinnamaldehyde acetal, bis(2-phenylethyl) anisaldehyde acetal, bis (citronellyl) cyclamen aldehyde acetal, and bis(citronellyl) citral acetal.

Non-limiting examples of optional ketals which are suitable for use in the fragrance delivery systems of the present invention include bis(linalyl) β -ionone ketal, bis(dihydromyrcenyl) α -damascone ketal, bis(linalyl) 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone ketal, bis(dihydromyrcenyl) β -ionone ketal, and bis(citronellyl) *cis*-jasmone ketal.

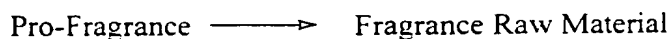
Non-limiting examples of optional β -ketoesters which are suitable for use in the fragrance delivery systems of the present invention include 2,6-dimethyl-7-octen-2-yl 3-(4-methoxyphenyl)-3-oxo-propionate, 3,7-dimethyl-1,6-octadien-3-yl 3-(α -naphthyl)-3-oxo-propionate, 2,6-dimethyl-7-octen-2-yl 3-(4-methoxyphenyl)-3-oxo-propionate, *cis* 3-hexen-1-yl 3-(β -naphthyl)-3-oxo-propionate, 2,6-dimethyl-7-octen-2-yl 3-(nonanyl)-3-oxo-propionate, 2,6-dimethyl-7-octen-2-yl 3-oxo-butyrate, 3,7-dimethyl-1,6-octadien-3-yl 3-oxo-butyrate, 2,6-dimethyl-7-octen-2-yl 3-(β -naphthyl)-3-oxo-2-methylpropionate, 3,7-dimethyl-1,6-octadien-3-yl 3-(β -naphthyl)-3-oxo-2,2-dimethylpropionate, 3,7-dimethyl-1,6-octadien-3-yl 3-(β -naphthyl)-3-oxo-2-methylpropionate, 3,7-dimethyl-2,6-octadienyl 3-(β -naphthyl)-3-oxo-propionate, and 3,7-dimethyl-2,6-octadienyl 3-heptyl-3-oxo-propionate.

Fragrance Release Half-life

One aspect of the present invention which is a key element in providing the formulator with a method for determining the manner in which a pro-fragrance according to the present invention releases its fragrance raw material, is the measurement of the pro-fragrance "Fragrance Release Half-Life, (FRHL). The pro-fragrances useful in the personal care compositions of the present invention generally have a delayed release of final fragrance raw material in order to achieve the increased fragrance longevity benefits described herein. However, the pro-fragrances generally also deliver the fragrance raw materials during a time period useful to the formulator, for example, within a time period desirable to the consumer.

For the purposes of the present invention the pro-accords generally have a FRHL of less than or equal to 12 hours when measured in NaH_2PO_4 buffer at pH 2.5 and greater than or equal to 0.1 hour when measured in NaH_2PO_4 buffer at pH 5.3. The "Fragrance Release Half-life" is defined herein as follows.

Pro-fragrances deliver their corresponding mixture of fragrance raw materials or fragrance accords according to the equation:



wherein the fragrance raw material which is released may be released as a single component or a multiple fragrance raw material accord.

The rate at which the fragrance is released is defined by the formula:

$$\text{Rate} = k[\text{Pro-fragrance}]$$

and can be further expressed by the formula:

$$-\frac{d[\text{Pro-fragrance}]}{dt} = k[\text{Pro-fragrance}]$$

wherein k is the release rate constant and $[\text{Pro-fragrance}]$ is the concentration of pro-fragrance. For the purposes of the present invention the "Fragrance Release Half-life", $t_{1/2}$, is related to the release rate constant by the formula:

$$t_{1/2} = \frac{0.693}{k}$$

and this relationship is used for the purposes of the present invention to determine the "FRHL".

Due to the hydrophobic nature of some pro-accords, it is necessary to conduct the determination of $t_{1/2}$ and k in a mixture of 90/10 dioxane/phosphate buffered water. The phosphate buffered water is prepared by admixing 3.95 mL of 85% phosphoric acid (H_3PO_4) and 24 g of sodium dihydrogen phosphate (NaH_2PO_4) with one liter of water. The pH of this solution is approximately 2.5. Next 10 mL of the phosphate buffer is admixed with 90 mL of dioxane and the pro-fragrance to be analyzed is added. The hydrolysis kinetics are then monitored by conventional HPLC at 30° C.

In some instances, it is desirable to formulate a fragrance delivery system having one or more pro-fragrances which deliver a rapid release of fragrance raw material in addition to the delayed onset of a fragrance. In such cases the hydrolysis rate, and therefore the determination of $t_{1/2}$ must be measured in a buffer system which can accommodate this more rapid hydrolysis rate.

The pro-fragrances of the present invention are stable under pH conditions encountered in the formulation and storage of fine perfume, personal care and personal hygiene articles which have a pH of from about 7.1 to 11.5, and during solution-use of such products. Due to their high molecular weight and hydrophobicity, these pro-fragrances and/or pro-accords remain deposited upon skin even when exposed to water (i.e. when formulated into a sun screen). Because the pro-fragrances are subject to hydrolysis when the pH is reduced, they hydrolyze to release their component fragrance compounds when applied to skin or are exposed even to reduced pH such as present in air and humidity. The reduction in pH should be at least 0.1, preferably at least about 0.5 units. Preferably the pH is reduced by at least 0.5 units to a pH of 7.5 or less, more preferably 6.9 or less. Preferably, the solution in which the pro-accord is applied is alkaline.

Odor Value

The pro-fragrances of the present invention typically have an Odor Value greater than or equal to about 1, preferably greater than or equal to about 5, more preferably greater than or equal to about 10. The term "Odor Value" is defined by the following formula:

$$OV = \frac{[\text{Concentration of FRM}]}{ODT}$$

wherein OV is the odor value of the fragrance raw material released upon the skin by the pro-accord. The odor value is the concentration of the fragrance raw material, FRM, on the skin surface divided by the Odor Detection Threshold, ODT. The term "level of noticeability" is often applied to and/or substituted for the term "odor value".

Odor Detection Threshold

For the purposes of the present invention the term "odor detection threshold" is defined as the level at which a fragrance raw material is perceptible to the average human. The odor detection threshold (ODT) of the compositions of the present invention are preferably measured by carefully controlled gas chromatograph (GC) conditions as described hereinbelow. The preferred fragrance raw materials of the present invention have an ODT of at least about 100 part per billion (ppb), more preferably 10 ppb, most preferably 1 ppb. Fragrance raw materials having an ODT greater than 10 parts per million (ppm) are typically avoided unless useful as an adjunct ingredient, for example, as an adjunct alcohol when adjusting the fragrance release half-life of an orthoester.

Determination of Odor Detection Thresholds is as follows. A gas chromatograph is characterized to determine the exact volume of material injected by a syringe, the precise split ratio, and the hydrocarbon response using a hydrocarbon standard of known concentration and chain-length distribution. The air flow rate is accurately measured and, assuming the duration of a human inhalation to last 0.02 minutes, the sampled volume is calculated. Since the precise concentration at the detector at any point in time is known, the mass per volume inhaled is known and hence the concentration of material. To determine whether a material has a threshold below 10 ppb, solutions are delivered to the sniff port at the back-calculated concentration. A panelist sniffs the GC effluent and identifies the retention time when odor is notice. The average over all panelists determines the threshold of noticeability or ODT. The necessary amount of analyte is injected onto the column to achieve a 10 ppb concentration at the detector. Typical gas chromatograph parameters for determining odor detection thresholds are listed below.

GC: 5890 Series II with FID detector 7673 Autosampler

Column: J&W Scientific DB-1, length 30 m. i.d. 0.25 mm. film thickness 1 μ m.

Split Injection: 17/1 split ratio

Autosampler: 1.13 μ l/injection

Column flow: 1.10 mL/min

Air flow: 345 mL/min

Inlet temperature: 245° C

Detector temperature: 285° C

Temperature Information:

Initial temperature: 50° C

Rate: 5° C/min

Final temperature: 280° C

Final time: 6 min

Leading assumptions: 0.02 minutes per sniff and that GC air adds to sample dilution.

Skin Performance Index

Although a pro-fragrance or pro-accord may comprise a fragrance release half-life which ensures delivery of a fragrance raw material during a period of time useful to the formulator, unless the fragrance raw materials which comprise said fragrance delivery system have ODT values large enough to be perceived by the user, the formulator will be compelled to use an inordinate amount of material to achieve a suitable fragrance level.

The pro-fragrances of the present invention have a Skin Performance Index (SPI) greater than or equal to 0.1, preferably greater than or equal to 0.5. The Skin Performance Index is defined by the following:

$$\text{SPI} = \frac{[\text{Odor Value}]^*}{t_{1/2}}$$

wherein the term [Odor Value]* is the estimated concentration of the fragrance raw material in the headspace above a solution of the fragrance raw material as measured in a 1% solution of ethanol, and $t_{1/2}$ is the fragrance release half-life measured at pH 5.3 in the above described buffer. For the purposes of the present invention, the $t_{1/2}$ of the SPI is measured at 5.3 and the value of the fragrance release half-life is preferably from 0.1 hours to 60 hours.

The [Odor Value]* is an estimation of the vapor pressure of the fragrance raw material using empirically determined KOVATS indices. "The Vapor Pressures of Pure Substances", T. Boublik et al., Elsevier, New York (1973) incorporated herein by reference, describes an index line for normal alkanes wherein C_{10} is equal to 30,000 ppb, C_{12} is equal to 3,000 ppb, C_{14} is equal to 300 ppb, C_{16} is equal to 30 ppb, etc. Using these values as reference standards, the KOVATS index of a fragrance raw material is obtained from gas chromatographic analysis of the FRM

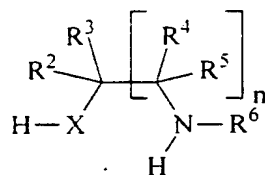
and the experimental index is then used to determine the relative vapor pressure and hence the head space concentration of the fragrance raw material.

"New Method for Estimating Vapor Pressure by the Use of Gas Chromatography" *J. Chromatography A*, 79 p 123-129, (1996) and "Simple and Versatile Injection System for Capillary Gas Chromatographic Columns: Performance Evaluation of a System Including Mass Spectrometric and Light Pipe Fourier-Transform Infrared Detection", *J. Chromatography A*, 713, p 201-215, (1996) included herein by reference, further describe methods and techniques suitable for use in determining the vapor pressure and head space concentration of FRM's as they relate to the term [Odor Value]* of the present invention.

Using the criteria set forth in the present invention *inter alia* fragrance release half-life, odor value, odor detection threshold, skin performance index, the formulator is able to fashion an aldehyde or ketone releasing cyclic pro-fragrance. By manipulation of the R², R³, R⁴, R⁵ and R⁶ units of the cyclic pro-fragrances of the present invention, the release rate of either an aldehyde or ketone fragrance raw material can be adjusted. Several different pro-fragrances which release the same fragrance raw material, but at differing rates or levels, can be admixed to further prolong or extend the period of fragrance raw material delivery.

The present invention also relates to a method for preparing a fragrance delivery system or a pro-fragrance component of a fragrance delivery system. In general, the process of the present invention comprises the steps of:

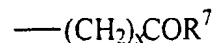
- a) admixing one or more precursors of the formula:



wherein X is oxygen or sulfur; each R², R³, R⁶ and each R⁴ and R⁵ pair are independently:

- a) hydrogen;
- b) C₁-C₁₀ substituted or unsubstituted linear alkyl;
- c) C₃-C₁₀ substituted or unsubstituted branched alkyl;
- d) C₂-C₁₀ substituted or unsubstituted linear alkenyl;
- e) C₃-C₁₀ substituted or unsubstituted branched alkenyl;
- f) C₃-C₁₅ substituted or unsubstituted cycloalkyl;
- g) C₄-C₁₅ substituted or unsubstituted branched cycloalkyl;

- i) C₃-C₁₅ substituted or unsubstituted branched cycloalkenyl;
- j) C₆-C₁₅ substituted or unsubstituted aryl;
- k) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- l) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;
- m) hydroxyl;
- n) a carbonyl comprising unit having the formula:

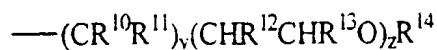


wherein R⁷ is:

- i) -OH;
- ii) -OR⁸ wherein R⁸ is hydrogen, C₁-C₁₅ substituted or unsubstituted linear alkyl, C₁-C₁₅ substituted or unsubstituted branched alkyl, C₂-C₂₂ substituted or unsubstituted linear alkenyl, C₃-C₂₂ substituted or unsubstituted branched alkenyl, or mixtures thereof;
- iii) -N(R⁹)₂ wherein R⁹ is hydrogen, C₁-C₆ substituted or unsubstituted linear alkyl, C₃-C₆ substituted or unsubstituted branched alkyl, or mixtures thereof;
- iv) C₁-C₂₂ substituted or unsubstituted linear alkyl;
- v) C₁-C₂₂ substituted or unsubstituted branched alkyl;
- vi) C₂-C₂₂ substituted or unsubstituted linear alkenyl;
- vii) C₃-C₂₂ substituted or unsubstituted branched alkenyl;
- viii) C₃-C₂₂ substituted or unsubstituted cycloalkyl;
- ix) C₆-C₂₂ substituted or unsubstituted aryl;
- x) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- xi) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;

the index x is from 0 to 22;

- o) alkyleneoxy units having the formula:



wherein each R¹⁰, R¹¹, and R¹² is independently;

- i) hydrogen;
- ii) -OH;
- iii) C₁-C₄ alkyl;

iv) or mixtures thereof;

R¹³ is:

i) hydrogen;

ii) C₁-C₄ alkyl;

iii) or mixtures thereof;

R¹⁴ is:

i) hydrogen;

ii) C₁-C₄ alkyl;

iii) or mixtures thereof;

R¹⁰ and R¹¹ can be taken together to form a C₃-C₆ spiroannulated ring, carbonyl unit, or mixtures thereof; y has the value from 0 to 10, z has the value from 1 to 50;

p) any two R², R³, R⁴, R⁵, or R⁶ units can be taken together to form:

i) a carbonyl moiety;

ii) a C₃-C₆ spiroannulated ring;

iii) a heterocyclic aromatic ring comprising from 5 to 7 atoms;

iv) a non-heterocyclic aromatic ring comprising from 5 to 7 atoms;

v) a heterocyclic ring comprising from 5 to 7 atoms;

vi) a non-heterocyclic ring comprising from 5 to 7 atoms;

vii) or mixtures thereof;

q) and mixtures thereof; and

the index n is an integer from 1 to 3; with one or more fragrance raw materials;

b) optionally adding a catalyst; and

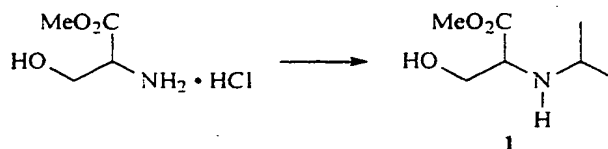
c) optionally isolating one or more heterocyclic pro-fragrance as described herein above.

The following are non-limiting examples of heterocyclic pro-fragrances according to the present invention. The pro-fragrances are obtained from single fragrance raw materials, or in the case of pro-fragrance libraries, the pro-fragrances are formed from an admixture of fragrance raw materials.

EXAMPLE I

Preparation of N-Isopropyl-DL-Serine Methyl Ester (1):

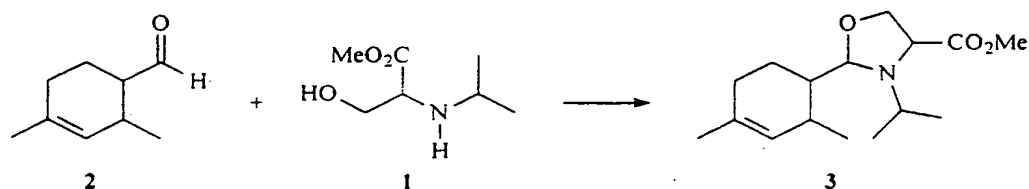
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To a slurry of 1 equivalent DL-serine methyl ester hydrochloride and 2 equivalents anhydrous sodium sulfate in methanol is added 1.05 equivalents sodium methoxide. The mixture is stirred at room temperature 5 minutes, after which 3 equivalents of acetone are added and the slurry is stirred overnight. The solids are removed by filtration and the excess acetone is removed from the filtrate under reduced pressure. Once the acetone is removed, platinum (IV) oxide (0.02 equivalents) is added. The slurry is stirred at room temperature 24 hours under a hydrogen atmosphere. The slurry is then filtered and the excess methanol is removed under reduced pressure. The residue is slurried in chloroform and filtered, and the filtrate is washed with dilute sodium bicarbonate, dried over anhydrous sodium sulfate, and filtered. Removal of chloroform under reduced pressure yields the desired product.

EXAMPLE 2

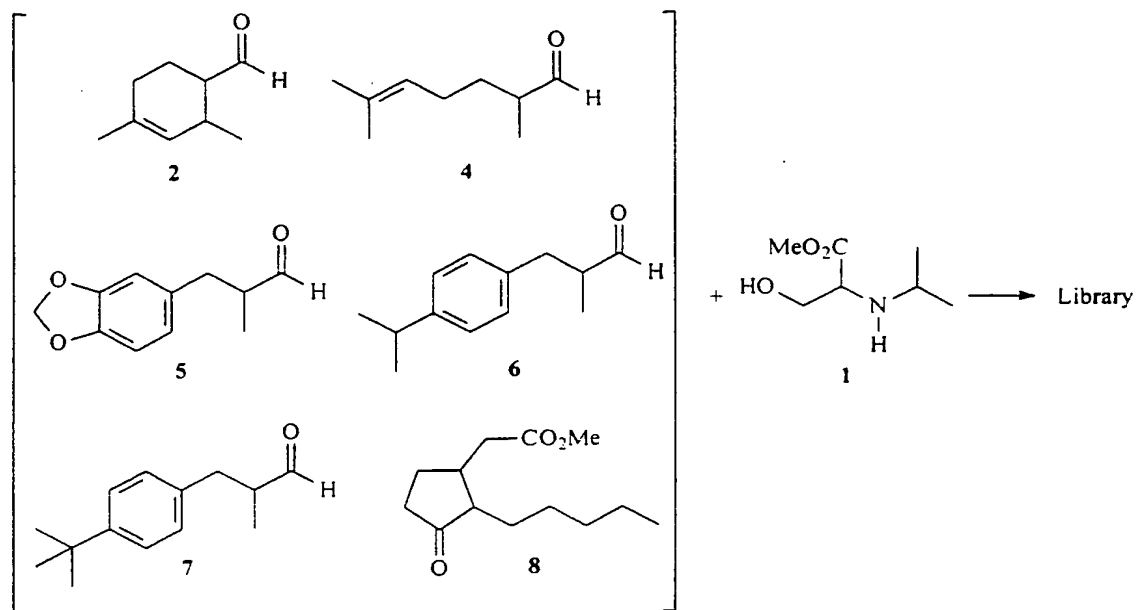
Preparation of Triplal-N-Isopropyl-DL-Serine Methyl Ester Oxazolidine (3):



A solution of triplal (2, 1.0 equiv), N-isopropyl-DL-serine methyl ester (1, 1.05 equiv) and 2,6-dichlorobenzoic acid (0.01 equiv) is refluxed 6 hours in toluene during which time water is removed by azeotropic distillation. The solution is cooled, washed with saturated sodium bicarbonate, dried over anhydrous sodium sulfate, and filtered. The toluene is subsequently removed under reduced pressure to yield the desired product, 3.

EXAMPLE 3

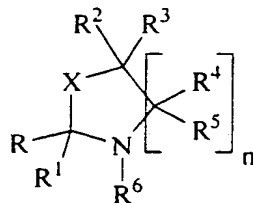
Preparation of an Oxazolidine Library from an Aldehyde/Ketone Admixture:



A slurry of 1.0 equiv each of triplal (2), melonal (4), helional (5), *pt*-bucinal (7), cymal (6) and hedione (8) is stirred for 2 weeks with N-isopropyl-DL-serine methyl ester (1, 6.3 equiv) and anhydrous sodium sulfate (12.0 equiv) at room temperature in anhydrous absolute ethanol. The sodium sulfate is removed by filtration to give the ethanolic solution of products. This solution is used without further purification. Alternatively, the ethanol may be removed under reduced pressure.

What is claimed is:

1. A pro-fragrance having the formula:



wherein said pro-fragrance or pro-accord releases an aldehyde or a ketone fragrance raw material, wherein X is oxygen or sulfur; R is:

- a) C₆-C₂₂ substituted or unsubstituted linear alkyl;
- b) C₆-C₂₂ substituted or unsubstituted branched alkyl;
- c) C₆-C₂₂ substituted or unsubstituted linear alkenyl;
- d) C₆-C₂₂ substituted or unsubstituted branched alkenyl;
- e) C₆-C₂₂ substituted or unsubstituted cycloalkyl;
- f) C₆-C₂₂ substituted or unsubstituted branched cycloalkyl;
- g) C₆-C₂₂ substituted or unsubstituted cycloalkenyl;
- h) C₆-C₂₂ substituted or unsubstituted branched cycloalkenyl;
- i) C₆-C₂₂ substituted or unsubstituted aryl;
- j) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- k) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;
- l) and mixtures thereof;

R¹ is:

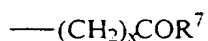
- a) hydrogen;
- b) C₁-C₁₀ substituted or unsubstituted linear alkyl;
- c) C₃-C₁₀ substituted or unsubstituted branched alkyl;
- d) C₂-C₁₀ substituted or unsubstituted linear alkenyl;
- e) C₃-C₁₀ substituted or unsubstituted branched alkenyl;
- f) C₃-C₁₅ substituted or unsubstituted cycloalkyl;
- g) C₄-C₁₅ substituted or unsubstituted branched cycloalkyl;
- h) C₄-C₁₅ substituted or unsubstituted cycloalkenyl;
- i) C₅-C₁₅ substituted or unsubstituted branched cycloalkenyl;
- j) C₆-C₁₅ substituted or unsubstituted aryl;

- k) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- l) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;
- m) and mixtures thereof;

R and R¹ can be taken together to form a substituted or unsubstituted ring having in the ring from 3 to 10 carbon atoms:

each R², R³, and each R⁴ and R⁵ pair are independently:

- a) R¹;
- b) hydroxyl;
- c) a carbonyl comprising unit having the formula:



wherein R⁷ is:

- i) -OH;
- ii) -OR⁸ wherein R⁸ is hydrogen, C₁-C₁₅ substituted or unsubstituted linear alkyl, C₁-C₁₅ substituted or unsubstituted branched alkyl, C₂-C₂₂ substituted or unsubstituted linear alkenyl, C₁-C₂₂ substituted or unsubstituted branched alkenyl, or mixtures thereof, wherein said substitution is not halogen;
- iii) -N(R⁹)₂ wherein R⁹ is hydrogen, C₁-C₆ substituted or unsubstituted linear alkyl, C₃-C₆ substituted or unsubstituted branched alkyl, or mixtures thereof;
- iv) C₁-C₂₂ substituted or unsubstituted linear alkyl;
- v) C₁-C₂₂ substituted or unsubstituted branched alkyl;
- vi) C₂-C₂₂ substituted or unsubstituted linear alkenyl;
- vii) C₃-C₂₂ substituted or unsubstituted branched alkenyl;
- viii) C₃-C₂₂ substituted or unsubstituted cycloalkyl;
- ix) C₆-C₂₂ substituted or unsubstituted aryl;
- x) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- xi) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;

the index x is from 1 to 22;

- d) alkyleneoxy units having the formula:



wherein each R¹⁰, R¹¹, and R¹² is independently:

- i) hydrogen;

- ii) -OH;
- iii) C₁-C₄ alkyl;
- iv) or mixtures thereof;

R¹³ is:

- i) hydrogen;
- ii) C₁-C₄ alkyl;
- iii) or mixtures thereof;

R¹⁴ is:

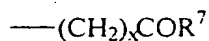
- i) hydrogen;
- ii) C₁-C₄ alkyl;
- iii) or mixtures thereof;

R¹⁰ and R¹¹ can be taken together to form a C₃-C₅ spiroannulated ring, carbonyl unit, or mixtures thereof; y has the value from 0 to 10, z has the value from 1 to 50;

- e) and mixtures thereof;

R⁶ is:

- a) C₁-C₁₀ substituted linear alkyl;
- b) C₃-C₁₀ substituted branched alkyl;
- c) C₂-C₁₀ substituted or unsubstituted linear alkenyl;
- d) C₃-C₁₀ substituted or unsubstituted branched alkenyl;
- e) C₃-C₁₅ substituted cycloalkyl;
- f) C₄-C₁₅ substituted or unsubstituted branched cycloalkyl;
- g) C₄-C₁₅ substituted or unsubstituted cycloalkenyl;
- h) C₅-C₁₅ substituted or unsubstituted branched cycloalkenyl;
- i) C₆-C₁₅ substituted aryl;
- j) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- k) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;
- l) a carbonyl comprising unit having the formula:



wherein R⁷ is:

- i) -OH;
- ii) -OR⁸ wherein R⁸ is hydrogen, C₁-C₁₅ substituted linear alkyl, C₁₁-C₁₅ unsubstituted linear alkyl, C₁-C₁₅ substituted branched alkyl, C₁₁-C₁₅

unsubstituted branched alkyl, C₂-C₂₂ substituted or unsubstituted linear alkenyl, C₃-C₂₂ substituted or unsubstituted branched alkenyl, or mixtures thereof, wherein said substitution is not halogen or thioalkyl;

- iii) -N(R⁹)₂ wherein R⁹ is hydrogen, C₁-C₆ substituted or unsubstituted linear alkyl, C₃-C₆ substituted or unsubstituted branched alkyl, or mixtures thereof;
- iv) C₁-C₂₂ substituted or unsubstituted linear alkyl;
- v) C₁-C₂₂ substituted or unsubstituted branched alkyl;
- vi) C₂-C₂₂ substituted or unsubstituted linear alkenyl;
- vii) C₃-C₂₂ substituted or unsubstituted branched alkenyl;
- viii) C₃-C₂₂ substituted or unsubstituted cycloalkyl;
- ix) C₆-C₂₂ substituted or unsubstituted aryl;
- x) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- xi) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;

the index x is from 0 to 22;

- m) alkyleneoxy units having the formula:



wherein each R¹⁰, R¹¹, and R¹² is independently;

- i) hydrogen;
- ii) -OH;
- iii) C₁-C₄ alkyl;
- iv) or mixtures thereof;

R¹³ is:

- i) hydrogen;
- ii) C₁-C₄ alkyl;
- iii) or mixtures thereof;

R¹⁴ is:

- i) hydrogen;
- ii) C₁-C₄ alkyl;
- iii) or mixtures thereof;

R¹⁰ and R¹¹ can be taken together to form a C₃-C₆ spiroannulated ring, carbonyl unit, or mixtures thereof; y has the value from 0 to 10, z has the value from 1 to 50;

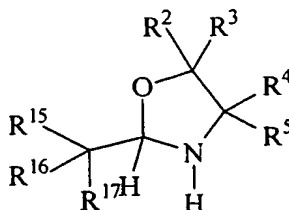
n) and mixtures thereof;

any two R^2 , R^3 , R^4 , R^5 , or R^6 units can be taken together to form:

- i) a carbonyl moiety;
- ii) a C_3 - C_6 spiroannulated ring;
- iii) a heterocyclic aromatic ring comprising from 5 to 7 atoms;
- iv) a non-heterocyclic aromatic ring comprising from 5 to 7 atoms;
- v) a heterocyclic ring comprising from 5 to 7 atoms;
- vi) a non-heterocyclic ring comprising from 5 to 7 atoms;
- vii) or mixtures thereof; and

the index n is an integer from 1 to 3.

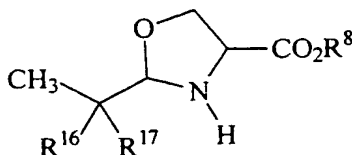
2. A compound according to Claim 1 wherein R is C_8 - C_{12} unsubstituted linear alkyl, C_8 - C_{12} unsubstituted branched alkyl, C_8 - C_{15} unsubstituted linear alkenyl, C_8 - C_{15} unsubstituted branched alkenyl, C_6 - C_{15} unsubstituted cycloalkyl, C_7 - C_{15} unsubstituted branched cycloalkyl, C_{10} - C_{20} unsubstituted cycloalkenyl, C_{10} - C_{20} unsubstituted branched cycloalkenyl, C_6 - C_{15} substituted or unsubstituted aryl, C_6 - C_{15} unsubstituted heterocyclicalkyl, and mixtures thereof, R^6 is hydrogen.
3. A compound according to either Claim 1 or 2 wherein said aldehyde which is released is selected from the group consisting of 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde, phenylacetaldehyde, methylnonyl acetaldehyde, 2-phenylpropan-1-al, 3-phenylprop-2-en-1-al, 3-phenyl-2-pentylprop-2-en-1-al, 3-phenyl-2-hexylprop-2-enal, 3-(4-isopropylphenyl)-2-methylpropan-1-al, 3-(4-ethylphenyl)-2,2-dimethylpropan-1-al, 3-(4-*tert*-butylphenyl)-2-methyl-propanal, 3-(3,4-methylenedioxyphenyl)-2-methylpropan-1-al, 3-(4-ethylphenyl)-2,2-dimethylpropanal, 3-(3-isopropylphenyl)butan-1-al, 2,6-dimethylhept-5-en-1-al, n-decanal, n-undecanal, n-dodecanal, 3,7-dimethyl-2,6-octadien-1-al, 4-methoxybenzaldehyde, 3-methoxy-4-hydroxybenz-aldehyde, 3-ethoxy-4-hydroxybenzaldehyde, 3,4-methylenedioxybenzaldehyde, 3,4-dimethoxybenzaldehyde, and mixtures thereof.
4. A compound according to any of Claims 1-3 having the formula:



wherein R^2 , R^3 , R^4 , and R^5 is the same as defined herein above, R^{15} , R^{16} , and R^{17} are each independently:

- a) C_1 - C_{22} substituted or unsubstituted linear alkyl, preferably methyl or ethyl, more preferably methyl;
- b) C_3 - C_{22} substituted or unsubstituted branched alkyl;
- c) C_2 - C_{22} substituted or unsubstituted linear alkenyl;
- d) C_3 - C_{22} substituted or unsubstituted branched alkenyl;
- e) C_3 - C_{22} substituted or unsubstituted cycloalkyl;
- f) C_4 - C_{22} substituted or unsubstituted branched cycloalkyl;
- g) C_4 - C_{22} substituted or unsubstituted cycloalkenyl;
- h) C_4 - C_{22} substituted or unsubstituted branched cycloalkenyl;
- i) C_6 - C_{22} substituted or unsubstituted aryl;
- j) C_6 - C_{22} substituted or unsubstituted heterocyclicalkyl;
- k) C_6 - C_{22} substituted or unsubstituted heterocyclicalkenyl;
- l) any two R^{15} , R^{16} , and R^{17} units can be taken together to form a substituted or unsubstituted ring having from 3-10 carbon atoms;
- m) and mixtures thereof.

5. A compound according to any of Claims 1-4 having the formula:

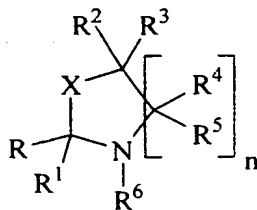


wherein R^8 is hydrogen, C_1 - C_{15} substituted linear alkyl, C_{11} - C_{15} unsubstituted linear alkyl, C_1 - C_{15} substituted branched alkyl, C_{11} - C_{15} unsubstituted branched alkyl, C_2 - C_{22} substituted or unsubstituted linear alkenyl, C_3 - C_{22} substituted or unsubstituted branched alkenyl, or mixtures thereof; R^{16} and R^{17} are each selected from the group consisting of methyl, C_6 - C_{15} substituted or unsubstituted alkylenearyl. R^{16} and R^{17} are taken together to form a substituted or unsubstituted cycloalkenyl ring, and mixtures thereof.

6. A fragrance delivery system comprising:

A) from 1% by weight, of a pro-fragrance component comprising:

- i) at least 1% by weight, of an aldehyde or ketone releasing pro-fragrance component, said pro-fragrance having the formula:



wherein said pro-fragrance or pro-accord releases an aldehyde or a ketone fragrance raw material, wherein X is oxygen or sulfur; R is:

- a) C₆-C₂₂ substituted or unsubstituted linear alkyl;
- b) C₆-C₂₂ substituted or unsubstituted branched alkyl;
- c) C₆-C₂₂ substituted or unsubstituted linear alkenyl;
- d) C₆-C₂₂ substituted or unsubstituted branched alkenyl;
- e) C₆-C₂₂ substituted or unsubstituted cycloalkyl;
- f) C₆-C₂₂ substituted or unsubstituted branched cycloalkyl;
- g) C₆-C₂₂ substituted or unsubstituted cycloalkenyl;
- h) C₆-C₂₂ substituted or unsubstituted branched cycloalkenyl;
- i) C₆-C₂₂ substituted or unsubstituted aryl;
- j) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- k) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;
- l) and mixtures thereof;

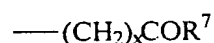
R¹ is:

- a) hydrogen;
- b) C₁-C₁₀ substituted or unsubstituted linear alkyl;
- c) C₃-C₁₀ substituted or unsubstituted branched alkyl;
- d) C₂-C₁₀ substituted or unsubstituted linear alkenyl;
- e) C₃-C₁₀ substituted or unsubstituted branched alkenyl;
- f) C₃-C₁₅ substituted or unsubstituted cycloalkyl;
- g) C₄-C₁₅ substituted or unsubstituted branched cycloalkyl;
- h) C₄-C₁₅ substituted or unsubstituted cycloalkenyl;

- i) C₅-C₁₅ substituted or unsubstituted branched cycloalkenyl;
- j) C₆-C₁₅ substituted or unsubstituted aryl;
- k) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- l) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;

R and R¹ can be taken together to form a substituted or unsubstituted ring having in the ring from 3 to 10 carbon atoms; and each R², R³, R⁶ and each R⁴ and R⁵ pair are independently:

- a) R¹;
- b) hydroxyl;
- c) a carbonyl comprising unit having the formula:



wherein R⁷ is:

- i) -OH;
- ii) -OR⁸ wherein R⁸ is hydrogen, C₁-C₁₅ substituted or unsubstituted linear alkyl, C₁-C₁₅ substituted or unsubstituted branched alkyl, C₂-C₂₂ substituted or unsubstituted linear alkenyl, C₃-C₂₂ substituted or unsubstituted branched alkenyl, or mixtures thereof;
- iii) -N(R⁹)₂ wherein R⁹ is hydrogen, C₁-C₆ substituted or unsubstituted linear alkyl, C₃-C₆ substituted or unsubstituted branched alkyl, or mixtures thereof;
- iv) C₁-C₂₂ substituted or unsubstituted linear alkyl;
- v) C₁-C₂₂ substituted or unsubstituted branched alkyl;
- vi) C₂-C₂₂ substituted or unsubstituted linear alkenyl;
- vii) C₃-C₂₂ substituted or unsubstituted branched alkenyl;
- viii) C₃-C₂₂ substituted or unsubstituted cycloalkyl;
- ix) C₆-C₂₂ substituted or unsubstituted aryl;
- x) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- xi) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;

the index x is from 0 to 22;

- d) alkyleneoxy units having the formula:



wherein each R¹⁰, R¹¹, and R¹² is independently;

- i) hydrogen;
- ii) -OH;
- iii) C₁-C₄ alkyl;
- iv) or mixtures thereof;

R¹³ is:

- i) hydrogen;
- ii) C₁-C₄ alkyl;
- iii) or mixtures thereof;

R¹⁴ is:

- i) hydrogen;
- ii) C₁-C₄ alkyl;
- iii) or mixtures thereof;

R¹⁰ and R¹¹ can be taken together to form a C₃-C₆ spiroannulated ring, carbonyl unit, or mixtures thereof; y has the value from 0 to 10, z has the value from 1 to 50;

- e) any two R², R³, R⁴, R⁵, or R⁶ units can be taken together to form:
 - i) a carbonyl moiety;
 - ii) a C₃-C₆ spiroannulated ring;
 - iii) a heterocyclic aromatic ring comprising from 5 to 7 atoms;
 - iv) a non-heterocyclic aromatic ring comprising from 5 to 7 atoms;
 - v) a heterocyclic ring comprising from 5 to 7 atoms;
 - vi) a non-heterocyclic ring comprising from 5 to 7 atoms;
 - vii) or mixtures thereof;
- f) and mixtures thereof; and

the index n is an integer from 1 to 3;

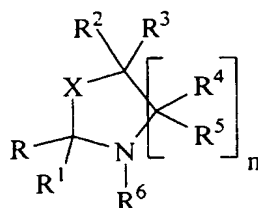
- ii) optionally from 1% by weight, of one or more pro-accords formed from at least one fragrance raw material, wherein said pro-accord is selected from the group consisting of acetals, ketals, orthoesters, orthocarbonates, and mixtures thereof, each pro-accord releasing upon hydrolysis said fragrance raw material from which it is formed, said fragrance raw materials selected from the group consisting of primary,

secondary, and tertiary alcohols, aldehydes, ketones, esters, carbonates, and mixtures thereof, provided each pro-accord:

- a) is formed from at least one fragrance raw material having a molecular weight greater than or equal to 100 g/mol;
 - b) has a fragrance release half-life of greater than or equal to 0.1 hours at pH 5.3 and less than or equal to 12 hours at pH 2.5 when measured in NaH_2PO_4 buffer;
 - iii) the balance carriers, stabilizers, and other adjunct ingredients: and
- B) optionally from 1% by weight, a fragrance raw material component comprising:
- i) optionally at least 1% by weight, of a mixture of one or more base note fragrances;
 - ii) optionally at least 1% by weight, of a mixture of one or more top or middle note fragrances;
 - iii) optionally the balance carriers, fixatives, and other adjunct ingredients.

7. A fine fragrance or perfume composition comprising:

- i) at least 0.01% by weight, of an aldehyde or ketone releasing pro-fragrance component, said pro-fragrance having the formula:



wherein said pro-fragrance or pro-accord releases an aldehyde or a ketone fragrance raw material, wherein X is oxygen or sulfur; R is:

- a) C_6 - C_{22} substituted or unsubstituted linear alkyl;
- b) C_6 - C_{22} substituted or unsubstituted branched alkyl;
- c) C_6 - C_{22} substituted or unsubstituted linear alkenyl;
- d) C_6 - C_{22} substituted or unsubstituted branched alkenyl;
- e) C_6 - C_{22} substituted or unsubstituted cycloalkyl;
- f) C_6 - C_{22} substituted or unsubstituted branched cycloalkyl;
- g) C_6 - C_{22} substituted or unsubstituted cycloalkenyl;
- h) C_6 - C_{22} substituted or unsubstituted branched cycloalkenyl;

- i) C₆-C₂₂ substituted or unsubstituted aryl;
- j) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- k) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;
- l) and mixtures thereof;

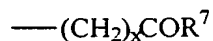
R¹ is:

- a) hydrogen;
- b) C₁-C₁₀ substituted or unsubstituted linear alkyl;
- c) C₃-C₁₀ substituted or unsubstituted branched alkyl;
- d) C₂-C₁₀ substituted or unsubstituted linear alkenyl;
- e) C₃-C₁₀ substituted or unsubstituted branched alkenyl;
- f) C₃-C₁₅ substituted or unsubstituted cycloalkyl;
- g) C₄-C₁₅ substituted or unsubstituted branched cycloalkyl;
- h) C₄-C₁₅ substituted or unsubstituted cycloalkenyl;
- i) C₅-C₁₅ substituted or unsubstituted branched cycloalkenyl;
- j) C₆-C₁₅ substituted or unsubstituted aryl;
- k) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- l) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;

R and R¹ can be taken together to form a substituted or unsubstituted ring having in the ring from 3 to 10 carbon atoms; and

each R², R³, R⁶ and each R⁴ and R⁵ pair are independently:

- a) R¹;
- b) hydroxyl;
- c) a carbonyl comprising unit having the formula:



wherein R⁷ is:

- i) -OH;
- ii) -OR⁸ wherein R⁸ is hydrogen, C₁-C₁₅ substituted or unsubstituted linear alkyl, C₁-C₁₅ substituted or unsubstituted branched alkyl, C₂-C₂₂ substituted or unsubstituted linear alkenyl, C₃-C₂₂ substituted or unsubstituted branched alkenyl, or mixtures thereof;

- iii) $-N(R^9)_2$ wherein R^9 is hydrogen, C_1-C_6 substituted or unsubstituted linear alkyl, C_3-C_6 substituted or unsubstituted branched alkyl, or mixtures thereof;
- iv) C_1-C_{22} substituted or unsubstituted linear alkyl;
- v) C_1-C_{22} substituted or unsubstituted branched alkyl;
- vi) C_2-C_{22} substituted or unsubstituted linear alkenyl;
- vii) C_3-C_{22} substituted or unsubstituted branched alkenyl;
- viii) C_3-C_{22} substituted or unsubstituted cycloalkyl;
- ix) C_6-C_{22} substituted or unsubstituted aryl;
- x) C_6-C_{22} substituted or unsubstituted heterocyclicalkyl;
- xi) C_6-C_{22} substituted or unsubstituted heterocyclicalkenyl;

the index x is from 0 to 22;

- d) alkyleneoxy units having the formula:



wherein each R^{10} , R^{11} , and R^{12} is independently:

- i) hydrogen;
- ii) $-OH$;
- iii) C_1-C_4 alkyl;
- iv) or mixtures thereof;

R^{13} is:

- i) hydrogen;
- ii) C_1-C_4 alkyl;
- iii) or mixtures thereof;

R^{14} is:

- i) hydrogen;
- ii) C_1-C_4 alkyl;
- iii) or mixtures thereof;

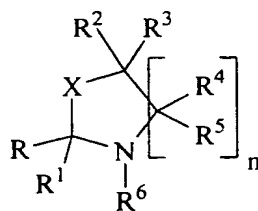
R^{10} and R^{11} can be taken together to form a C_3-C_6 spiroannulated ring, carbonyl unit, or mixtures thereof; y has the value from 0 to 10, z has the value from 1 to 50;

- e) any two R^2 , R^3 , R^4 , R^5 , or R^6 units can be taken together to form:
- i) a carbonyl moiety;
 - ii) a C_3-C_6 spiroannulated ring;

- iii) a heterocyclic aromatic ring comprising from 5 to 7 atoms;
 - iv) a non-heterocyclic aromatic ring comprising from 5 to 7 atoms;
 - v) a heterocyclic ring comprising from 5 to 7 atoms;
 - vi) a non-heterocyclic ring comprising from 5 to 7 atoms;
 - vii) or mixtures thereof;
 - f) and mixtures thereof; and
- the index n is an integer from 1 to 3;
- ii) optionally from 1% by weight, of one or more pro-accords which comprise n fragrance raw materials but which release $n+1$ fragrance raw materials;
 - iii) optionally from 1% by weight, of one or more pro-fragrances selected from the group consisting of acetals, ketals, orthoesters, orthocarbonate, β -ketoesters, and mixtures thereof;
 - iv) optionally from 1% by weight, of one or more fragrance raw materials; and
 - v) optionally one or more carriers, fixatives, stabilizers, or adjunct ingredients.

8. A perfume composition having extended fragrance character impressions comprising:

- A) a pro-accord component comprising:
 - i) at least 0.01% by weight, of an aldehyde or ketone releasing pro-fragrance component, said pro-fragrance having the formula:



wherein said pro-fragrance or pro-accord releases an aldehyde or a ketone fragrance raw material, wherein X is oxygen or sulfur; R is:

- a) C_6-C_{22} substituted or unsubstituted linear alkyl;
- b) C_6-C_{22} substituted or unsubstituted branched alkyl;
- c) C_6-C_{22} substituted or unsubstituted linear alkenyl;
- d) C_6-C_{22} substituted or unsubstituted branched alkenyl;
- e) C_6-C_{22} substituted or unsubstituted cycloalkyl;
- f) C_6-C_{22} substituted or unsubstituted branched cycloalkyl;
- g) C_6-C_{22} substituted or unsubstituted cycloalkenyl;

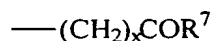
- h) C₆-C₂₂ substituted or unsubstituted branched cycloalkenyl;
- i) C₆-C₂₂ substituted or unsubstituted aryl;
- j) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- k) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;
- l) and mixtures thereof;

R¹ is:

- a) hydrogen;
- b) C₁-C₁₀ substituted or unsubstituted linear alkyl;
- c) C₃-C₁₀ substituted or unsubstituted branched alkyl;
- d) C₂-C₁₀ substituted or unsubstituted linear alkenyl;
- e) C₃-C₁₀ substituted or unsubstituted branched alkenyl;
- f) C₃-C₁₅ substituted or unsubstituted cycloalkyl;
- g) C₄-C₁₅ substituted or unsubstituted branched cycloalkyl;
- h) C₄-C₁₅ substituted or unsubstituted cycloalkenyl;
- i) C₅-C₁₅ substituted or unsubstituted branched cycloalkenyl;
- j) C₆-C₁₅ substituted or unsubstituted aryl;
- k) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- l) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;

R and R¹ can be taken together to form a substituted or unsubstituted ring having in the ring from 3 to 10 carbon atoms; and each R², R³, R⁶ and each R⁴ and R⁵ pair are independently:

- a) R¹;
- b) hydroxyl;
- c) a carbonyl comprising unit having the formula:



wherein R⁷ is:

- i) -OH;
- ii) -OR⁸ wherein R⁸ is hydrogen, C₁-C₁₅ substituted or unsubstituted linear alkyl, C₁-C₁₅ substituted or unsubstituted branched alkyl, C₂-C₂₂ substituted or unsubstituted linear alkenyl, C₃-C₂₂ substituted or unsubstituted branched alkenyl, or mixtures thereof;

- iii) $-N(R^9)_2$ wherein R^9 is hydrogen, C_1 - C_6 substituted or unsubstituted linear alkyl, C_3 - C_6 substituted or unsubstituted branched alkyl, or mixtures thereof;
 - iv) C_1 - C_{22} substituted or unsubstituted linear alkyl;
 - v) C_1 - C_{22} substituted or unsubstituted branched alkyl;
 - vi) C_2 - C_{22} substituted or unsubstituted linear alkenyl;
 - vii) C_3 - C_{22} substituted or unsubstituted branched alkenyl;
 - viii) C_3 - C_{22} substituted or unsubstituted cycloalkyl;
 - ix) C_6 - C_{22} substituted or unsubstituted aryl;
 - x) C_6 - C_{22} substituted or unsubstituted heterocyclicalkyl;
 - xi) C_6 - C_{22} substituted or unsubstituted heterocyclicalkenyl;
- the index x is from 0 to 22;

d) alkyleneoxy units having the formula:



wherein each R^{10} , R^{11} , and R^{12} is independently;

- i) hydrogen;
- ii) $-OH$;
- iii) C_1 - C_4 alkyl;
- iv) or mixtures thereof;

R^{13} is:

- i) hydrogen;
- ii) C_1 - C_4 alkyl;
- iii) or mixtures thereof;

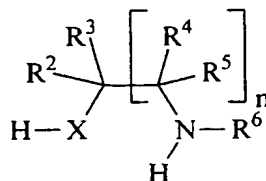
R^{14} is:

- i) hydrogen;
- ii) C_1 - C_4 alkyl;
- iii) or mixtures thereof;

R^{10} and R^{11} can be taken together to form a C_3 - C_6 spiroannulated ring, carbonyl unit, or mixtures thereof; y has the value from 0 to 10, z has the value from 1 to 50;

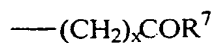
- e) any two R^2 , R^3 , R^4 , R^5 , or R^6 units can be taken together to form:
 - i) a carbonyl moiety;
 - ii) a C_3 - C_6 spiroannulated ring;

- iii) a heterocyclic aromatic ring comprising from 5 to 7 atoms;
 - iv) a non-heterocyclic aromatic ring comprising from 5 to 7 atoms;
 - v) a heterocyclic ring comprising from 5 to 7 atoms;
 - vi) a non-heterocyclic ring comprising from 5 to 7 atoms;
 - vii) or mixtures thereof;
 - f) and mixtures thereof; and
the index n is an integer from 1 to 3;
 - ii) from 0.1% by weight, of one or more pro-accords formed from at least one fragrance raw material, wherein said pro-accord is selected from the group consisting of acetals, ketals, orthoesters, orthocarbonates, and mixtures thereof, each pro-accord releasing upon hydrolysis said fragrance raw material from which it is formed, said fragrance raw materials selected from the group consisting of primary, secondary, and tertiary alcohols, aldehydes, ketones, esters, carbonates, and mixtures thereof, provided each pro-accord:
 - a) is formed from at least one fragrance raw material having a molecular weight greater than or equal to 100 g/mol;
 - b) has a fragrance release half-life of greater than or equal to 0.1 hours at pH 5.3 and less than or equal to 12 hours at pH 2.5 when measured in NaH_2PO_4 buffer;
 - iii) the balance carriers, stabilizers, and other adjunct ingredients; and
 - B) a fragrance raw material component comprising:
 - i) a mixture of base note fragrances;
 - ii) one or more top or middle note fragrances;
 - ii) the balance carriers, fixatives, and other adjunct ingredients.
9. A method for preparing a fragrance delivery system or a pro-fragrance component of a fragrance delivery system comprises the steps of:
- a) admixing one or more precursors of the formula:



wherein X is oxygen or sulfur; each R^2 , R^3 , R^6 and each R^4 and R^5 pair are independently:

- a) hydrogen;
- b) C_1 - C_{10} substituted or unsubstituted linear alkyl;
- c) C_3 - C_{10} substituted or unsubstituted branched alkyl;
- d) C_2 - C_{10} substituted or unsubstituted linear alkenyl;
- e) C_3 - C_{10} substituted or unsubstituted branched alkenyl;
- f) C_3 - C_{15} substituted or unsubstituted cycloalkyl;
- g) C_4 - C_{15} substituted or unsubstituted branched cycloalkyl;
- h) C_4 - C_{15} substituted or unsubstituted cycloalkenyl;
- i) C_5 - C_{15} substituted or unsubstituted branched cycloalkenyl;
- j) C_6 - C_{15} substituted or unsubstituted aryl;
- k) C_6 - C_{22} substituted or unsubstituted heterocyclicalkyl;
- l) C_6 - C_{22} substituted or unsubstituted heterocyclicalkenyl;
- m) hydroxyl;
- n) a carbonyl comprising unit having the formula:



wherein R^7 is:

- i) $-\text{OH}$;
- ii) $-\text{OR}^8$ wherein R^8 is hydrogen, C_1 - C_{15} substituted or unsubstituted linear alkyl, C_1 - C_{15} substituted or unsubstituted branched alkyl, C_2 - C_{22} substituted or unsubstituted linear alkenyl, C_3 - C_{22} substituted or unsubstituted branched alkenyl, or mixtures thereof;
- iii) $-\text{N}(\text{R}^9)_2$ wherein R^9 is hydrogen, C_1 - C_6 substituted or unsubstituted linear alkyl, C_3 - C_6 substituted or unsubstituted branched alkyl, or mixtures thereof;
- iv) C_1 - C_{22} substituted or unsubstituted linear alkyl;
- v) C_1 - C_{22} substituted or unsubstituted branched alkyl;

- vi) C₂-C₂₂ substituted or unsubstituted linear alkenyl;
- vii) C₃-C₂₂ substituted or unsubstituted branched alkenyl;
- viii) C₃-C₂₂ substituted or unsubstituted cycloalkyl;
- ix) C₆-C₂₂ substituted or unsubstituted aryl;
- x) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- xi) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;

the index x is from 0 to 22;

- o) alkyleneoxy units having the formula:



wherein each R¹⁰, R¹¹, and R¹² is independently:

- i) hydrogen;
- ii) -OH;
- iii) C₁-C₄ alkyl;
- iv) or mixtures thereof;

R¹³ is:

- i) hydrogen;
- ii) C₁-C₄ alkyl;
- iii) or mixtures thereof;

R¹⁴ is:

- i) hydrogen;
- ii) C₁-C₄ alkyl;
- iii) or mixtures thereof;

R¹⁰ and R¹¹ can be taken together to form a C₃-C₆ spiroannulated ring, carbonyl unit, or mixtures thereof; y has the value from 0 to 10, z has the value from 1 to 50;

- p) any two R², R³, R⁴, R⁵, or R⁶ units can be taken together to form:

- i) a carbonyl moiety;
- ii) a C₃-C₆ spiroannulated ring;
- iii) a heterocyclic aromatic ring comprising from 5 to 7 atoms;
- iv) a non-heterocyclic aromatic ring comprising from 5 to 7 atoms;
- v) a heterocyclic ring comprising from 5 to 7 atoms;
- vi) a non-heterocyclic ring comprising from 5 to 7 atoms;
- vii) or mixtures thereof;

- q) and mixtures thereof; and
the index n is an integer from 1 to 3; with one or more fragrance raw materials;
- b) optionally adding a catalyst; and
- c) optionally isolating one or more heterocyclic pro-fragrances.